# Durability and CMAS Resistance of Advanced Environmental Barrier Coatings Systems for SiC/SiC Ceramic Matrix Composites

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# Environmental Barrier Coating - CMAS Interaction Research Efforts

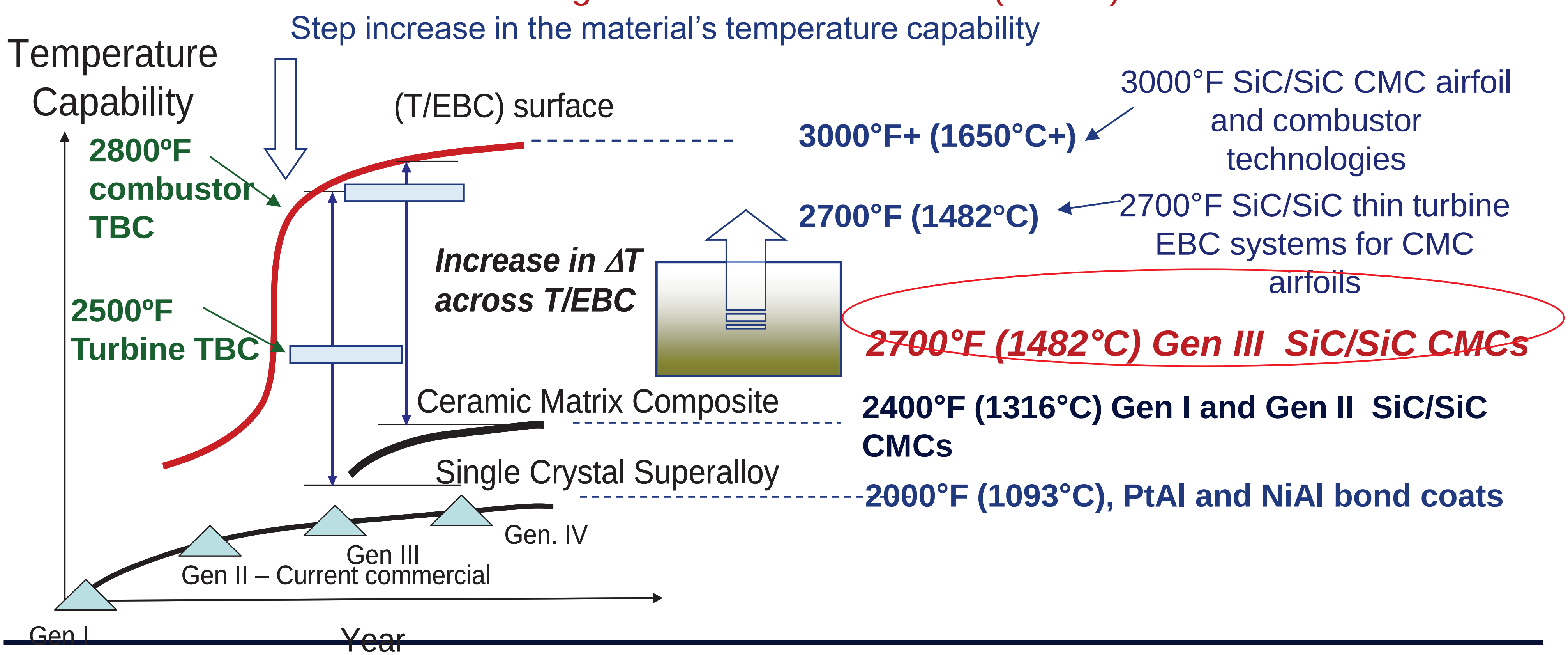
- Advanced EBC development – composition design and developments for improved CMAS resistance; thermomechanical-CMAS Interactions and durability – Zhu et al
- NASA-Air Force Venture and Viper Turbine Coating-CMAS Collaborative programs - Zhu, James Smialek, Robert A. Miller, Bryan Harder
- Formal NASA Intern Undergraduate Students – Nadia Ahlborg and Dan Miladinovich
- Fundamental NASA in-house CMAS properties - Narottam Bansal and Valerie Weiner

# Outline

- **Environmental barrier coating (EBC) development: the CMAS relevance**
- **Some generalized CMAS related failures**
- **CMAS degradation of environmental barrier coating (EBC) systems: rare earth silicates**
  - Ytterbium silicate and yttrium silicate EBCs
  - Some reactions, kinetics and mechanisms
- **Advanced EBCs, $HfO_2$- and Rare Earth - Silicon based 2700°F+ capable bond coats**
- **Summary**

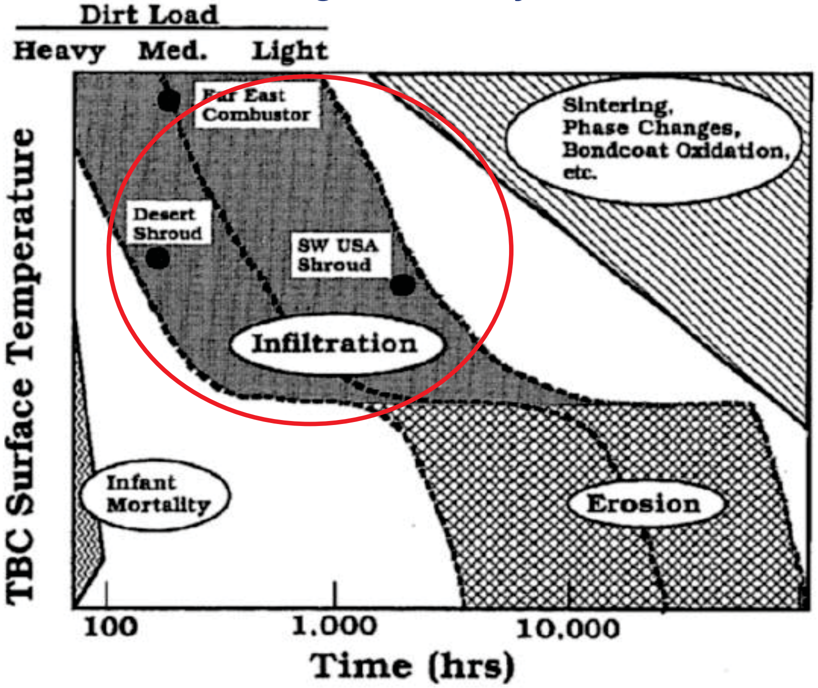
# NASA Environmental Barrier Coatings (EBCs) and Ceramic Matrix Composite (CMC) System Development

- **Emphasize material temperature capability, performance and *long-term* durability-** Highly loaded EBC-CMCs with temperature capability of 2700°F (1482°C)
  - 2700-3000°F (1482-1650°C) turbine and CMC combustor coatings
  - 2700°F (1482°C) EBC bond coat technology for supporting next generation
    - Recession: <5 mg/cm$^2$ per 1000 h
    - Coating and component strength requirements: 15-30 ksi, or 100- 207 Mpa
    - Resistance to Calcium Magnesium Alumino-Silicate (CMAS)

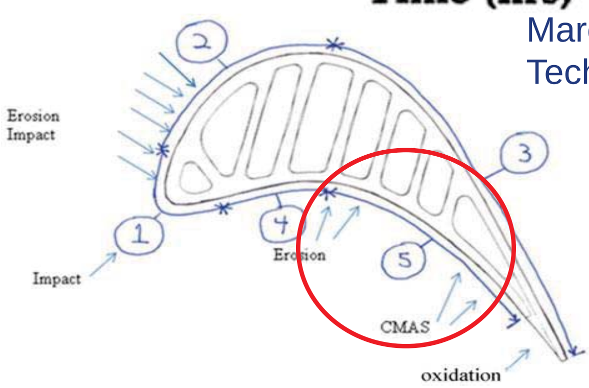


# EBC-CMAS Degradation is of Concern with Increasing Operating Temperatures

- **Emphasize improving temperature capability, performance and *long-term* durability of ceramic turbine airfoils**
  - Increased gas inlet temperatures for net generation engines lead to significant CMAS -related coating durability issues – CMAS infiltration and reactions




Marcus P. Borom et al, Surf. Coat. Technol. 86-87, 1996

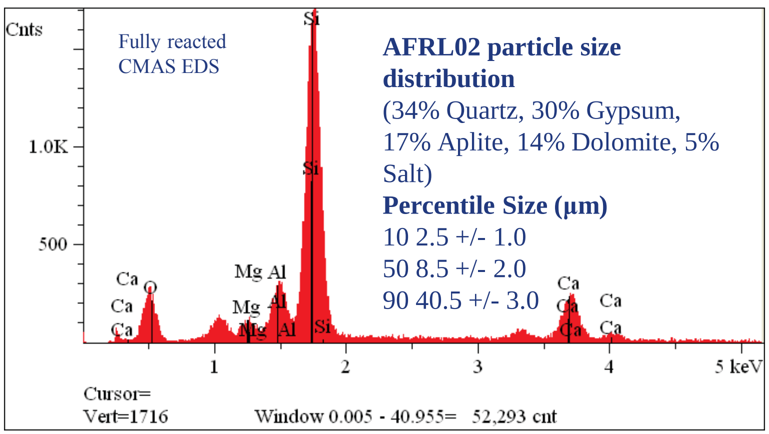


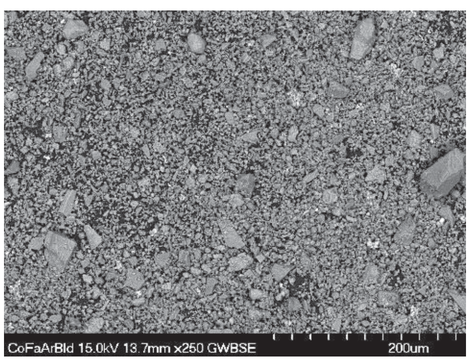

Current airfoil CMAS attack region - R. Darolia, International Materials Reviews, 2013

# Calcium Magnesium Alumino-Silicate (CMAS) Systems Used in Laboratory Tests

- Synthetic CMAS compositions, in particular, NASA modified version (NASA CMAS), and the Air Force Powder Technology Incorporated PTI 02 CMAS currently being used
- Saudi Sands used for past turbine coating studies
- CMAS $SiO_2$ content typically ranging from 43-49 mole%; such as NASA's CMAS (with NiO and FeO)
- Collaborations on-going with the Air Force; also planned DLR, ONERA etc on Volcanic Ash Composition selections

## ARFL PTI 11717A 02 used at NASA for CMAS studies

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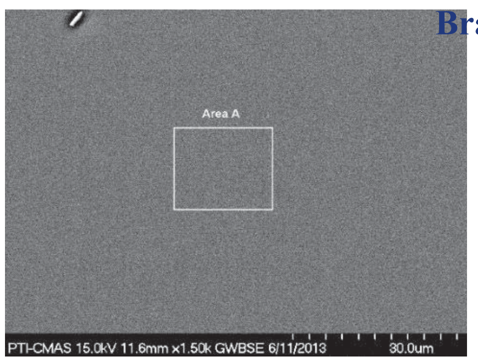



Fully reacted

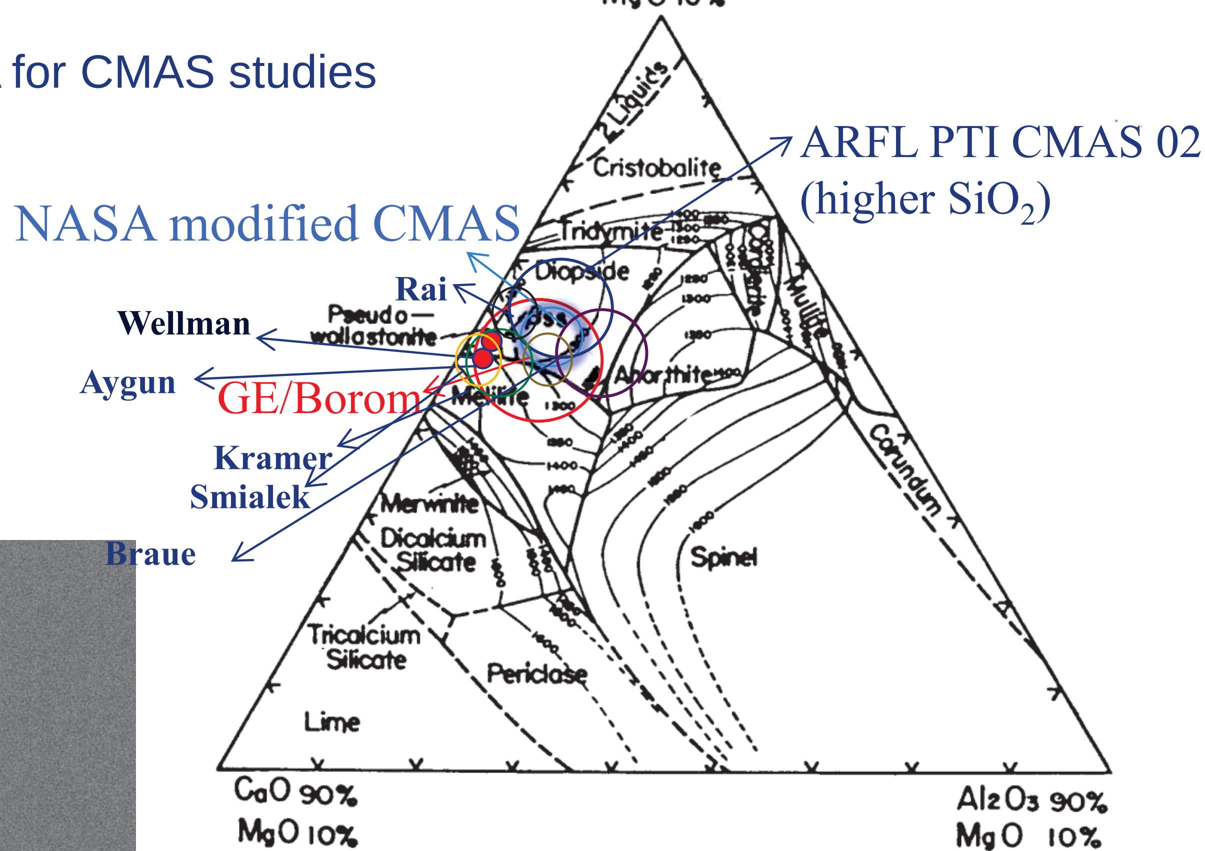
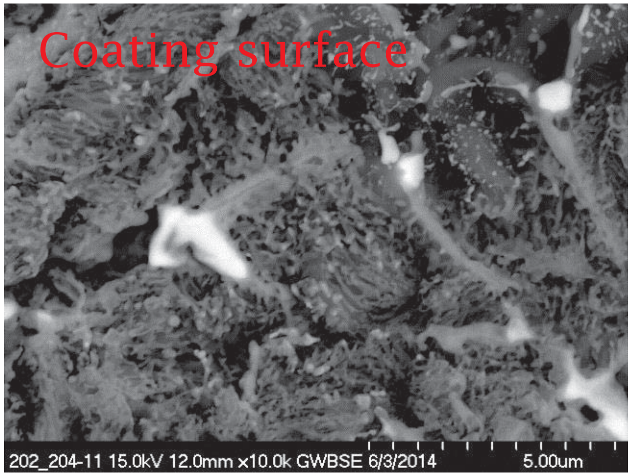


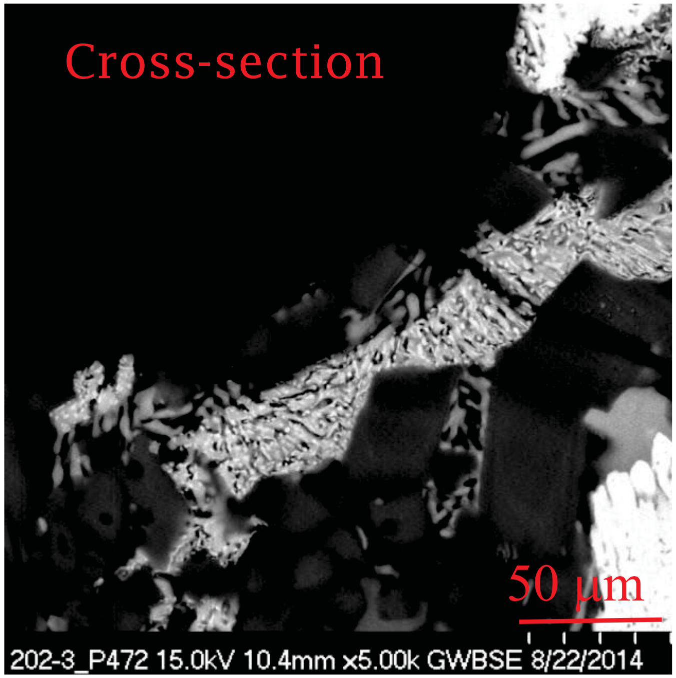

Fig. 4. The 10% MgO plane of the system CaO–MgO–$Al_2O_3$–$SiO_2$ showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

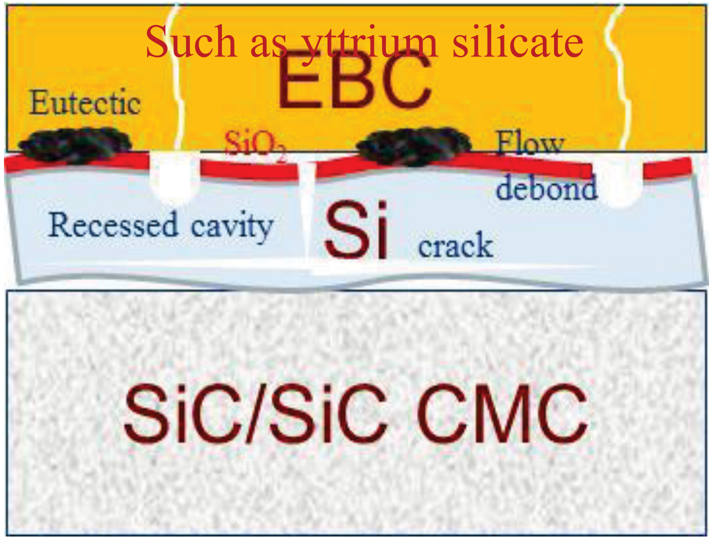
# CMAS Related Degradations in EBCs

## – CMAS effects

- Significantly reduce melting points of the EBCs and bond coats
- Cause more severe degradations with thin airfoil EBCs
- CMAS increase EBC diffusivities and permeability, thus less protective as an environmental barrier
- Reduced mechanical properties: such as strength and toughness reductions
- Leads to grain boundary attack thus disintegrate EBCs
- CMAS interactions with heat flux, thermal cycling, erosion and thermomechanical fatigue



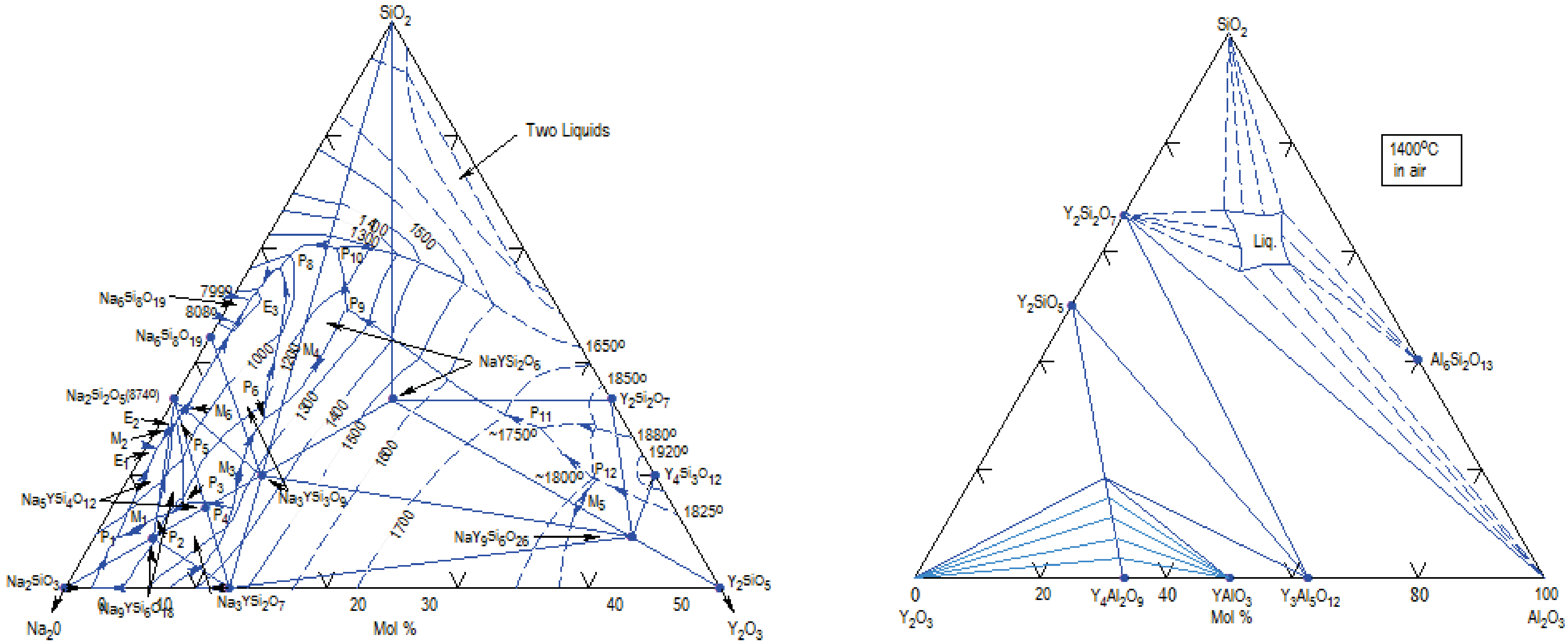

EBC and degradations

CMAS induced melting and failure

# CMAS Related Degradations in EBCs - Continued

– **CMAS effects on EBC temperature capability**

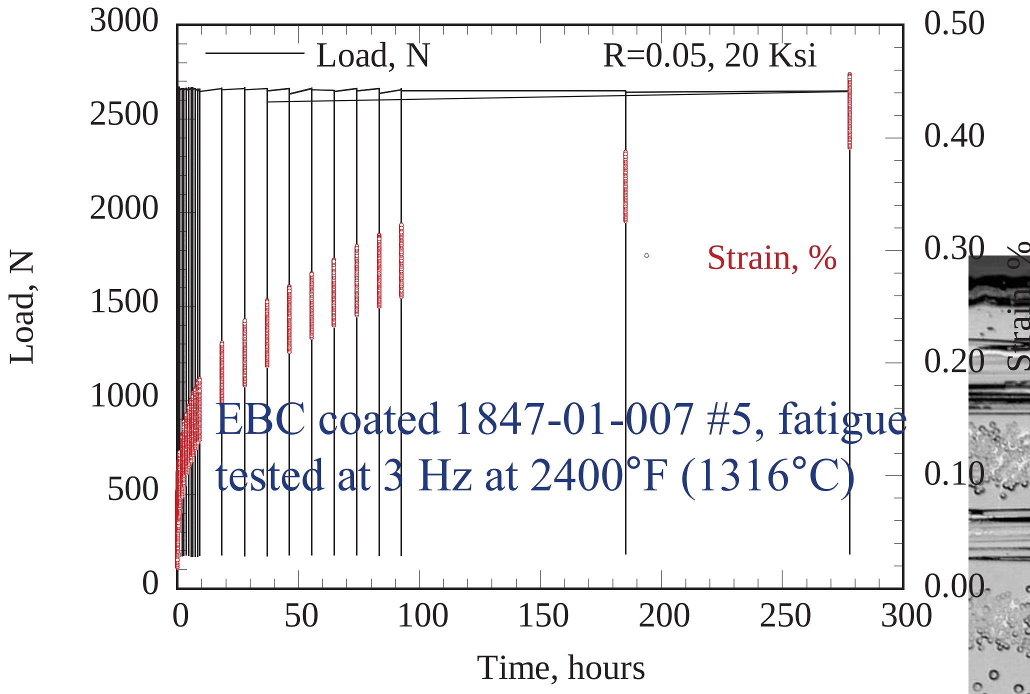
- Silicate reactions with $NaO_2$ and $Al_2O_3$ silicate

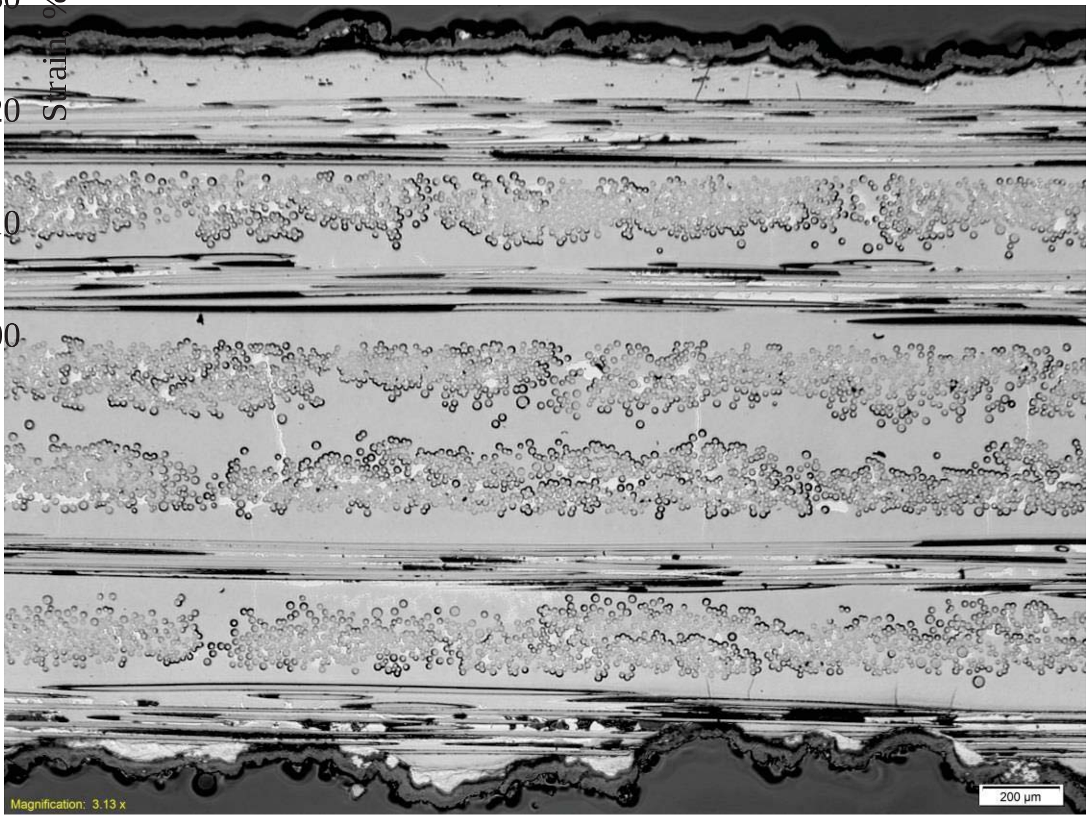



Phase diagrams showing yttrium di-silicate reactions with $SiO_2$, NaO and $Al_2O_3$

# CMAS Related Degradations in EBCs

- **Fatigue – environmental interaction is of great concern**




A 20 micrometer thick EBC bond coated Prepreg SiC/SiC CMC after 40 hr, 20 Ksi, stress ratio R=0.05 fatigue testing in air

# Environmental Barrier Coating Development Limitations and Requirements

- Current EBCs limited in their temperature capability, water vapor stability and long-term durability, especially for advanced high pressure, high bypass turbine engines

- Advanced EBCs also require higher strength and toughness
  - In particular, resistance to combined high-heat-flux, engine high pressure, combustion environment, creep-fatigue, loading interactions

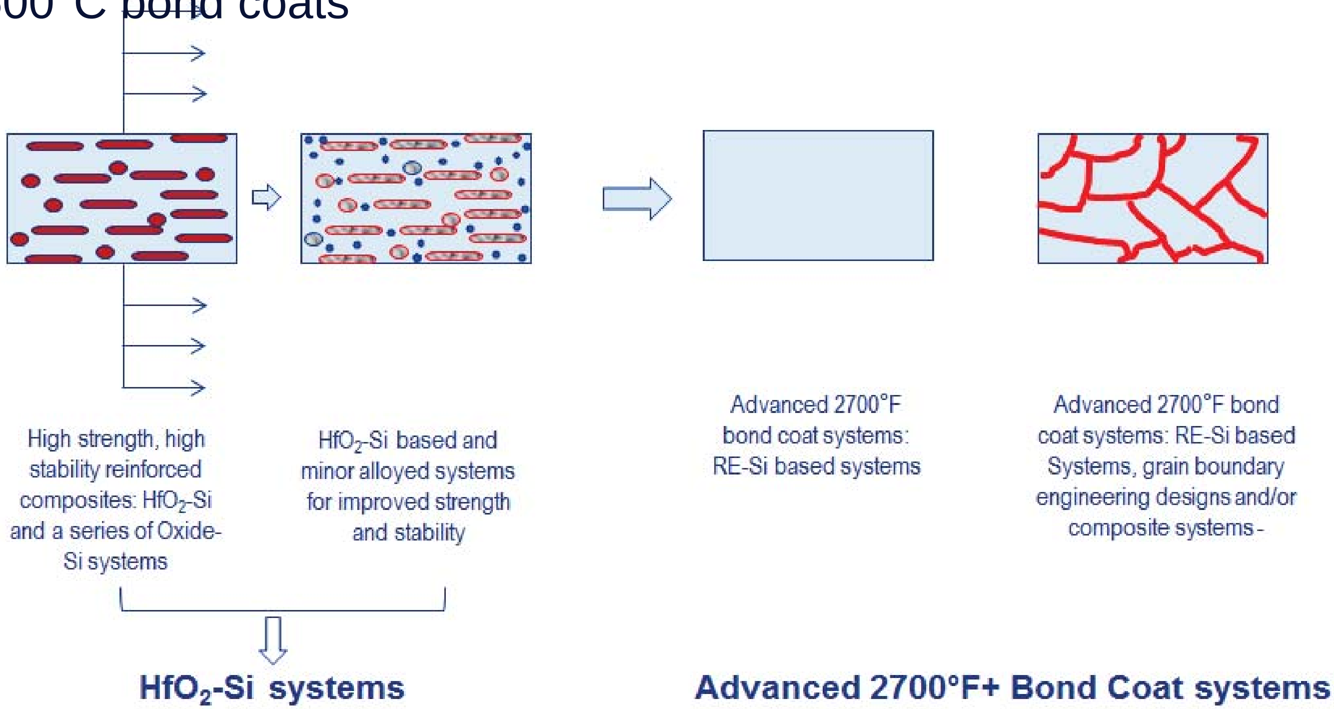
- EBCs need improved erosion, impact and calcium-magnesium-alumino-silicate (CMAS) resistance and interface stability
  - Critical to reduce the EBC Si/$SiO_2$ reactivity and their concentration tolerance

- EBC-CMC systems need advanced processing for realizing complex coating compositions, architectures and thin turbine configurations for next generation high performance engines
  - Advanced high temperature processing of high stability cluster and nano-composites

# NASA EBC Systems

NASA EBC Systems

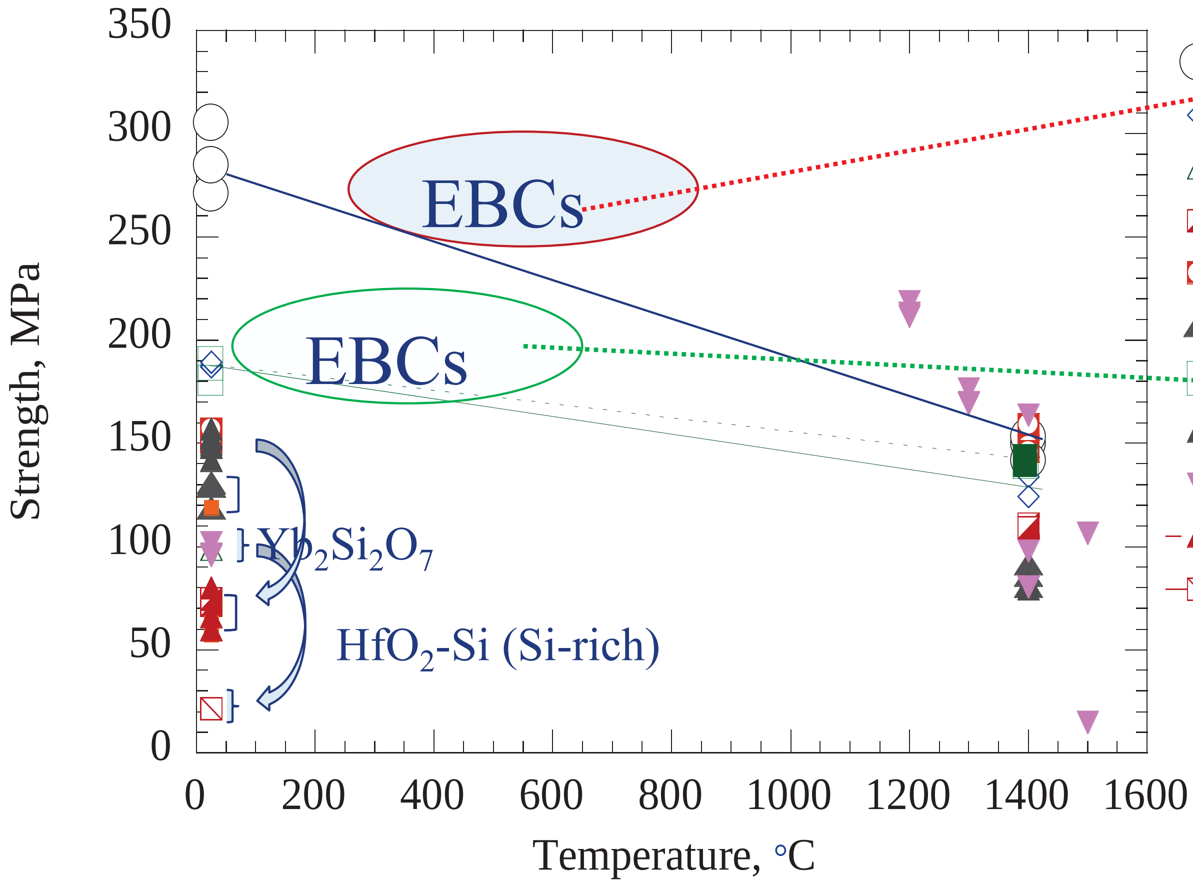
- $HfO_2$ -$RE_2O_3$-$SiO_2$/$RE_2Si_{2\text{-}x}O_{7\text{-}2x}$ environmental barrier systems
  - Controlled silica content and transition element and rare earth dopants to improve EBC stability and toughness
  - Develop $HfO_2$-Si based + X (dopants) and more advanced rare earth composite compound composition systems for 2700°F+ long-term applications
  - Develop prime-reliant composite EBC-CMC interfaces for fully integrated EBC-bond coat systems
- $RE_2O_3$-$SiO_2$-$Al_2O_3$ Systems
- Develop advanced NASA high toughness alternating layered systems
- Advanced 1500°C bond coats



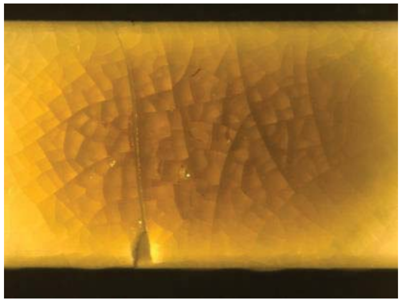
# Strength Results of Selected EBC and EBC Bond Coats - CMAS Reaction resulted in Strength Reduction in Silicates

Selected EBC systems

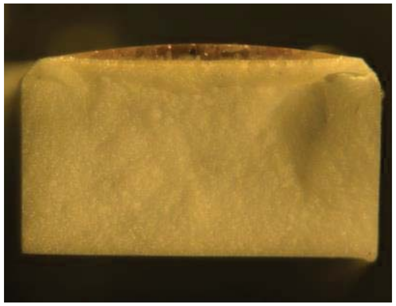
- $HfO_2$-RE-Si, along with co-doped rare earth silicates and rare earth alumino-silicates , for optimized strength, stability and temperature capability
- CMAS infiltrations can reduce the strength




Strength test data compared



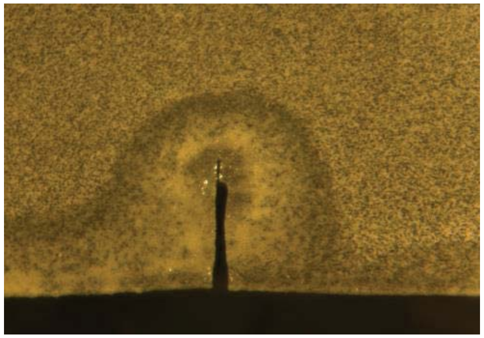
$Yb_2Si_2O_7$ CMAS reacted tensile surface



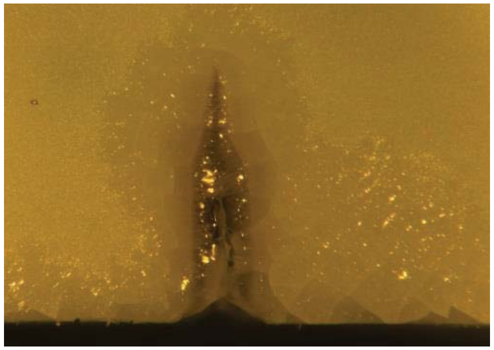
$Yb_2Si_2O_7$ CMAS reacted specimen fracture surface

# Effect of CMAS Reaction on Toughness of $HfO_2$-Si Bond Coat and $Yb_2Si_2O_7$ EBC

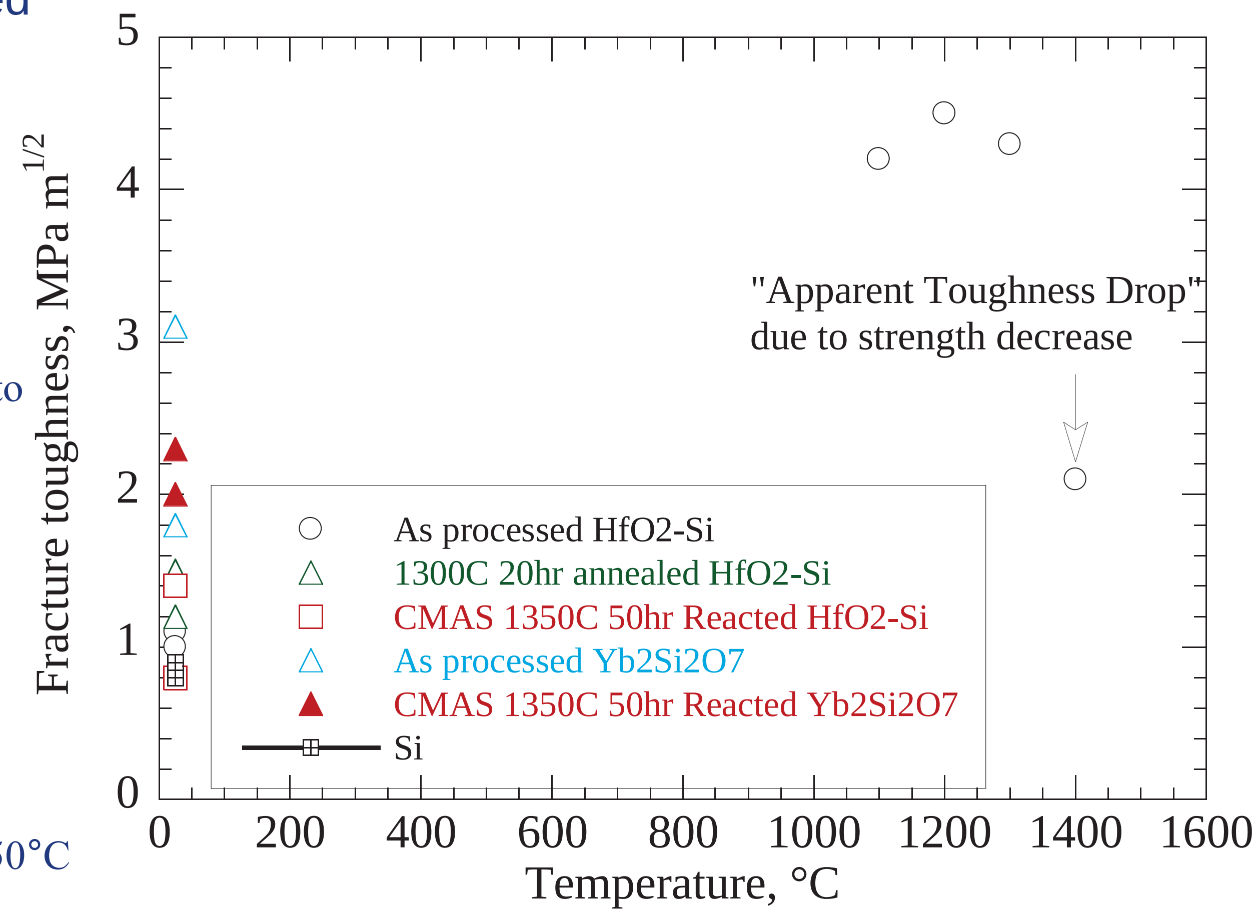
- $HfO_2$-Si bond coat and ytterbium di-silicate fracture toughness studied
  - $HfO_2$-Si toughness >4-5 MPa $m^{1/2}$ achieved at higher temperature
  - Annealing heat treatments at 1300°C improved lower temperature toughness
  - CMAS effect unclear due to the compounded effects of possible 1350°C CMAS reaction degradation and annealing
- Ytterbium silicate EBC toughness may also be reduced due to CMAS reactions
  - More measurements are needed



$HfO_2$-Si illustrating notch distortion due to CMAS exposure at 1350°C for 50 hrs

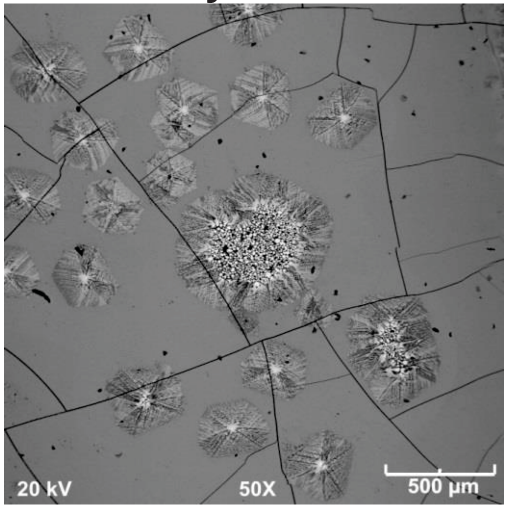


$Yb_2Si_2O_7$ notch after CMAS exposure at 1350°C for 50 hrs

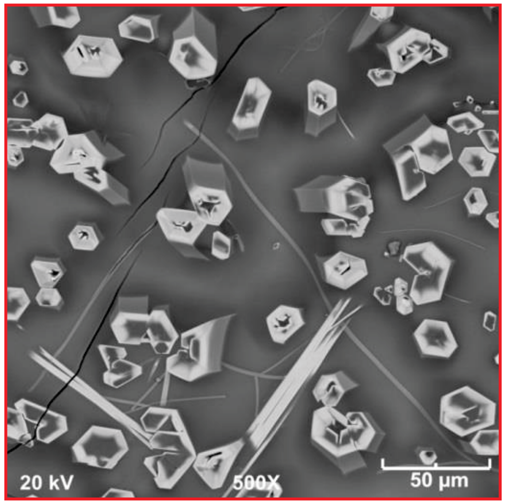


# EBC CMAS Surface Reactions

– Ytterbium- and yttrium-disilicate silicates reactions and dissolutions in CAMS




Ytterbium silicate surface CMAS melts: 50 hr 1300°C



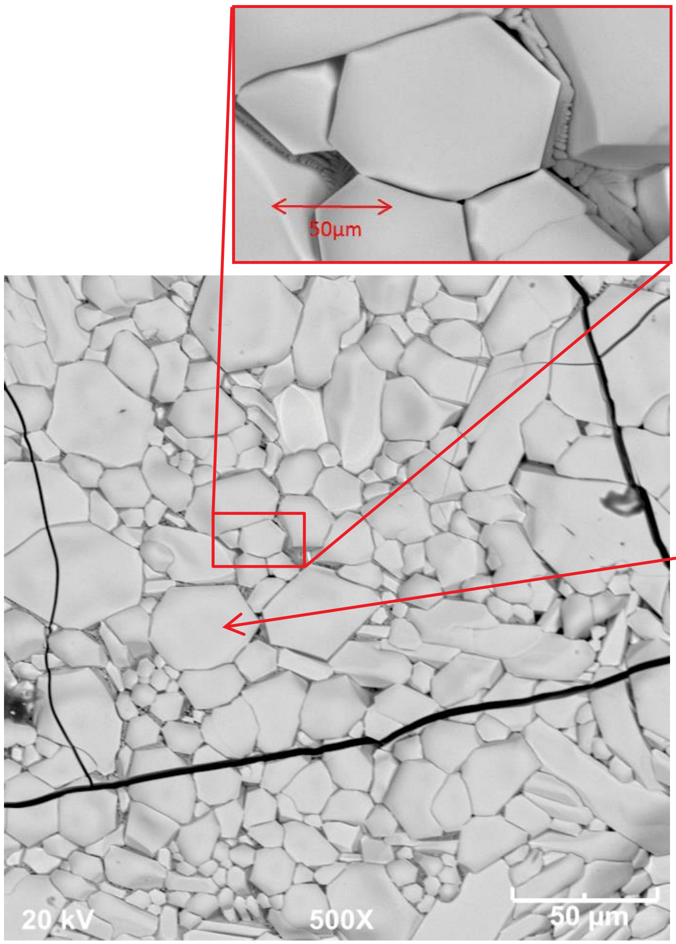

Ytterbium silicate surface CMAS melts: 5 hr 1500°C


Yttrium silicate surface CMAS melts: 50 hr 1300°C

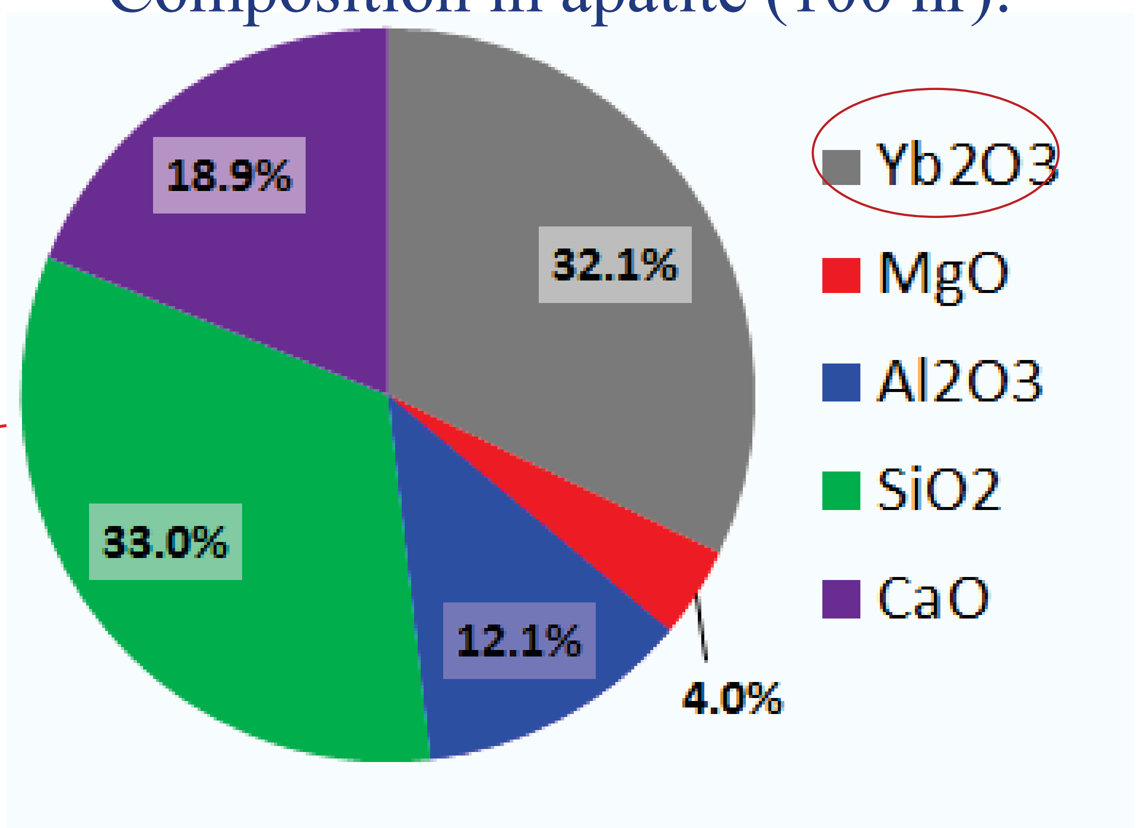
Yttrium silicate surface CMAS melts: 5 hr 1500°C

# EBC Reacted Apatite Phases under Long-Term Testing at 1500°C – Ytterbium silicate EBC

- Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases
- Difference in partitioning of ytterbium vs. yttrium in apatite




Composition in apatite (100 hr):

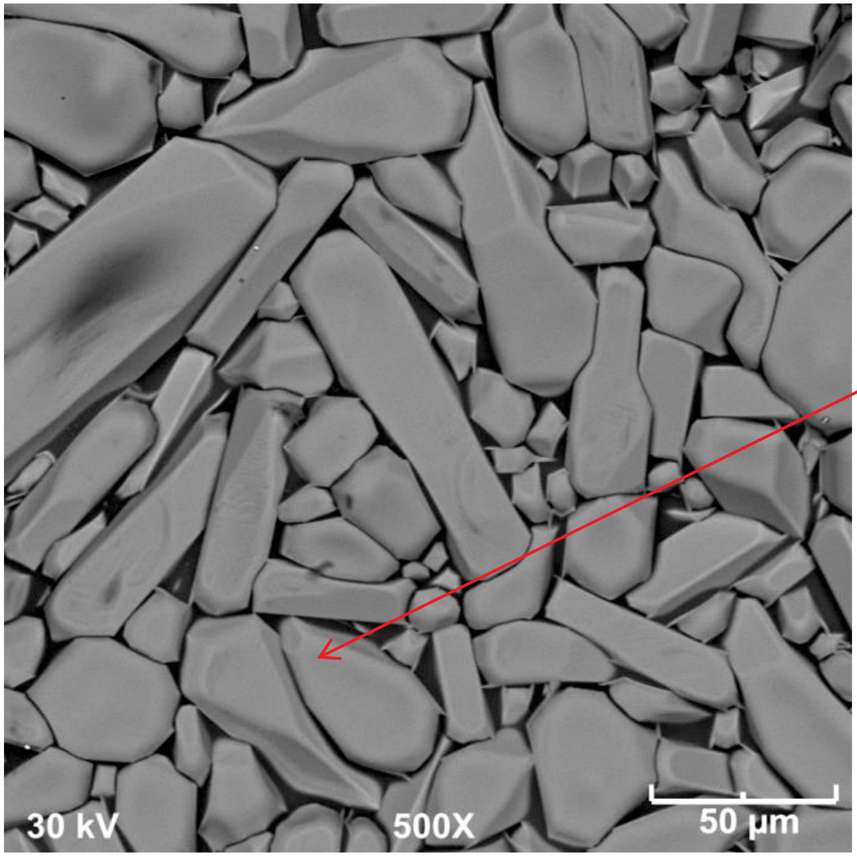


# EBC Reacted Apatite Phases under Long-Term Testing at 1500°C: Yttrium Silicate EBC

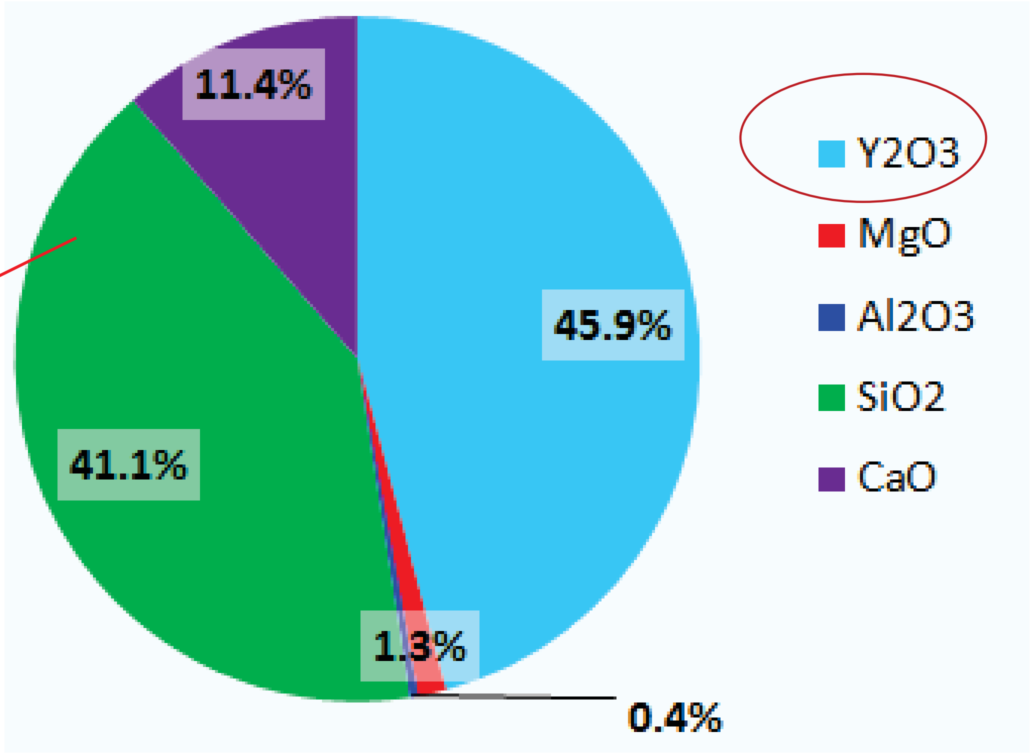
– Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases

– Difference in partition of ytterbium vs. yttrium

- Average AEO/$RE_2O_3$ ratio ~ 0.68 for ytterbium silicate – CMAS system
- Average AEO/$RE_2O_3$ ratio ~ 0.22 for yttrium silicate – CMAS system

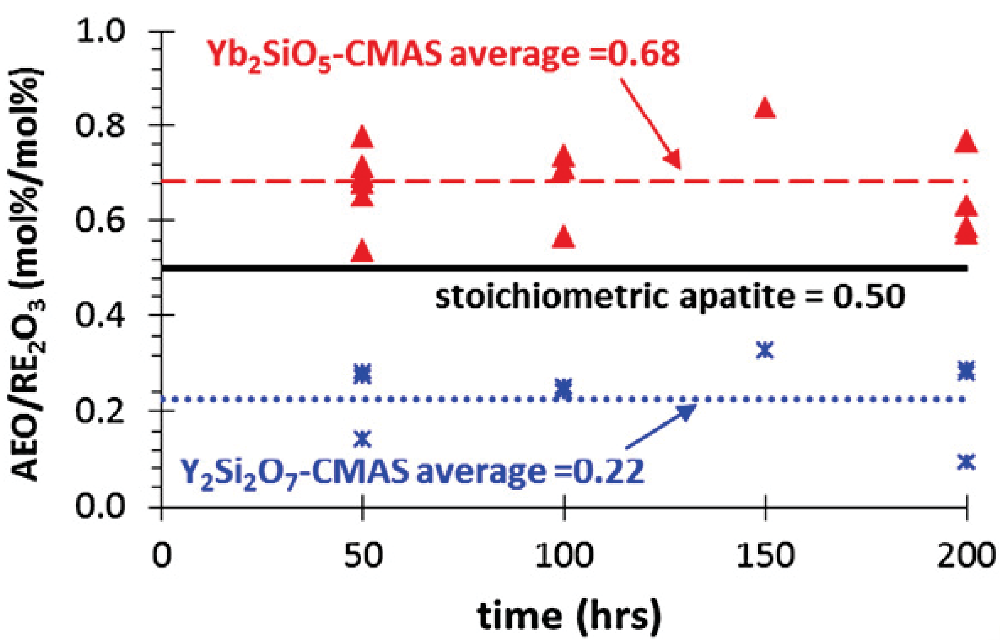



## Composition in apatite (100 hr):

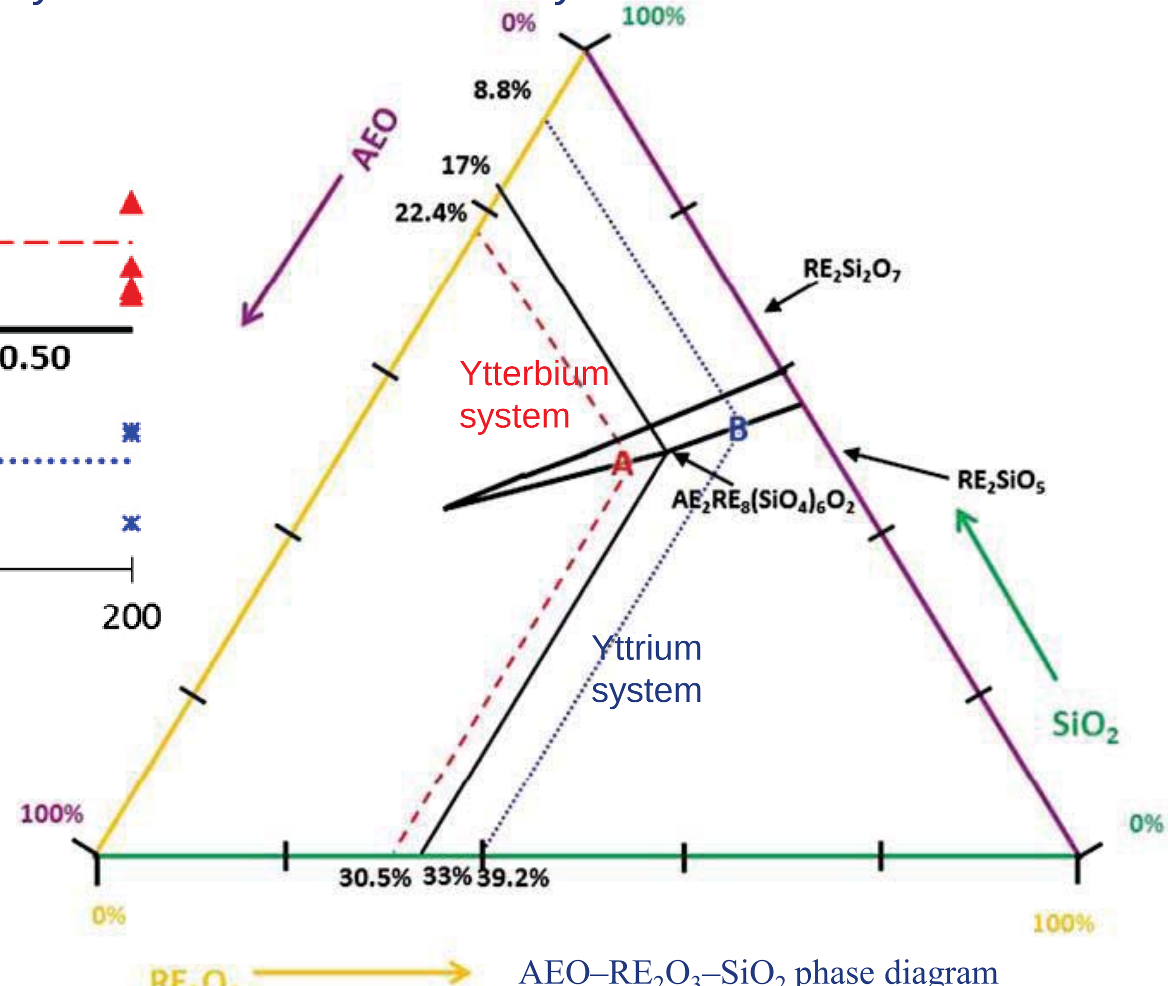


# Stoichiometry of the Reacted Apatite Phases under Long-Term Testing at 1500°C

– Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases – up to 200 hr testing
– Difference in partitioning of ytterbium vs. yttrium in apatite
  - Average AEO/$RE_2O_3$ ratio ~ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/$RE_2O_3$ ratio ~ 0.22 for yttrium silicate – CMAS system



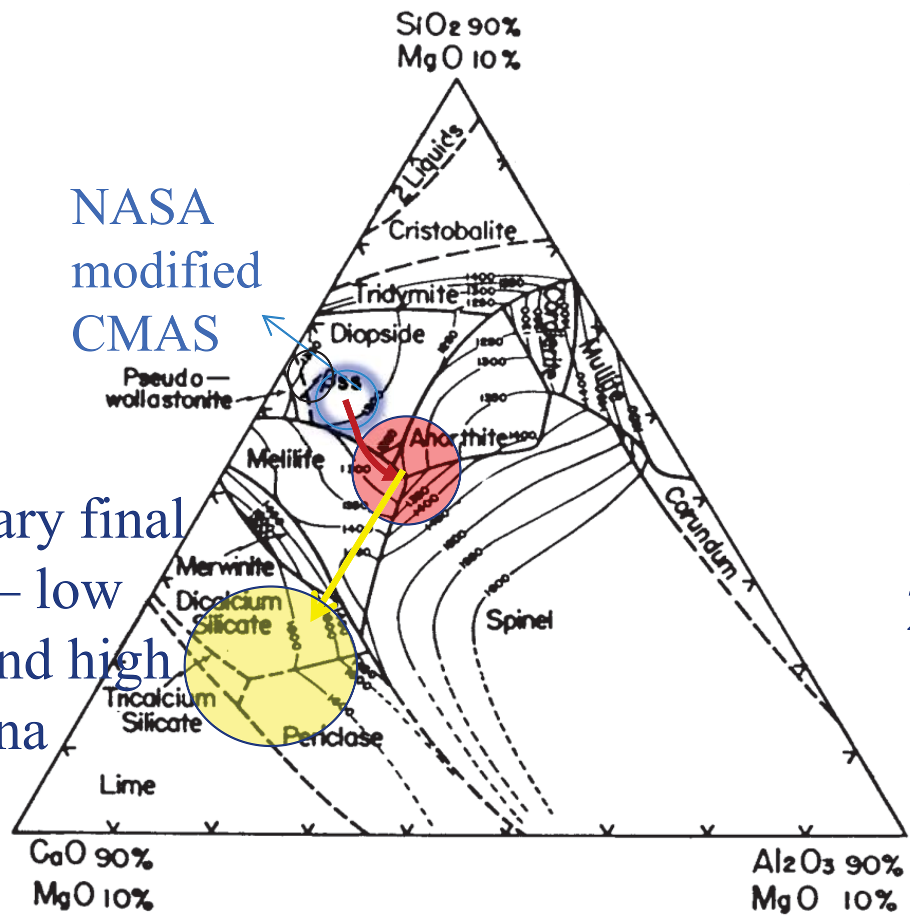

Ahlborg and Zhu, Surface & Coatings Technology 237 (2013) 79–87.




AEO–$RE_2O_3$–$SiO_2$ phase diagram

# Effect of CMAS Reactions on Grain Boundary Phases

– CMAS and grain boundary phase has higher $Al_2O_3$ content (17-22 mole%)
  - Eutectic region with high $Al_2O_3$ content ~1200°C melting
  - Loss of $SiO_2$ due to volatility

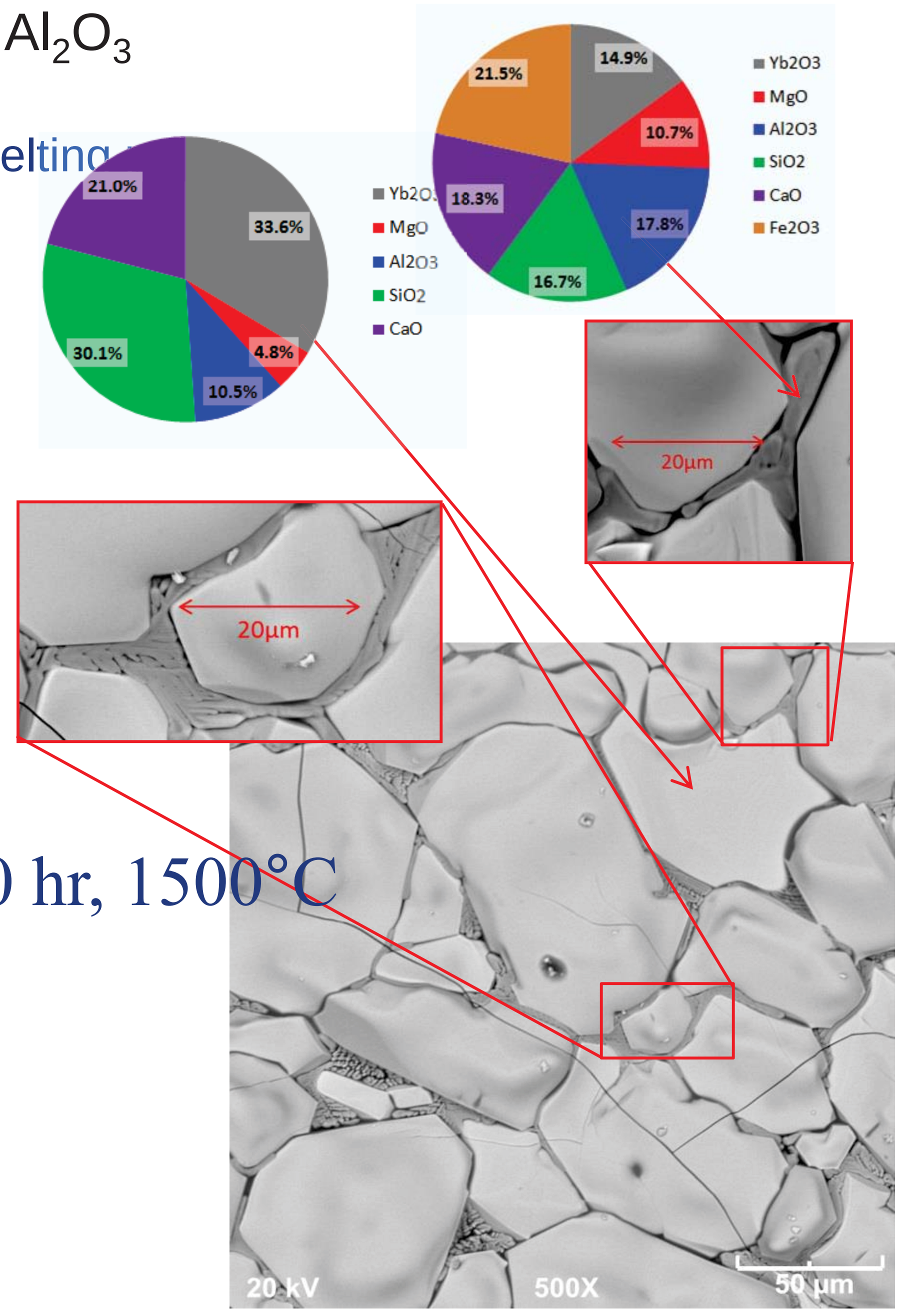



NASA modified CMAS

Grain boundary final phase – low $SiO_2$ and high Alumina

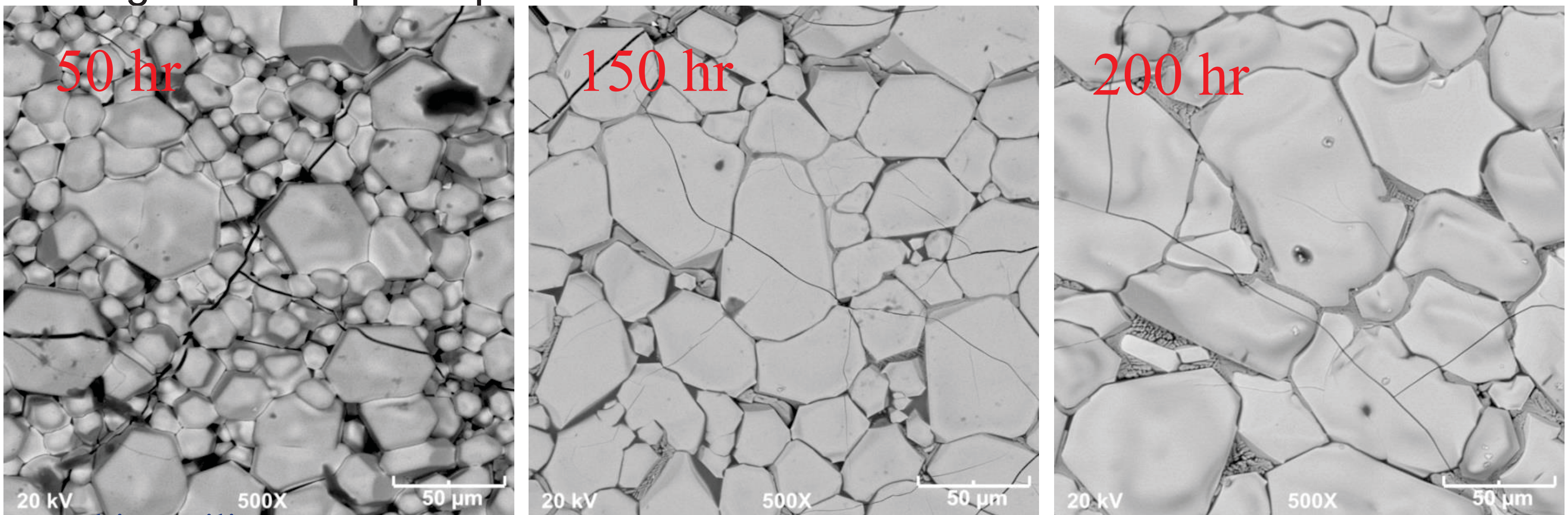
Fig. 4. The 10% MgO plane of the system $CaO–MgO–Al_2O_3–SiO_2$ showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

200 hr, 1500°C

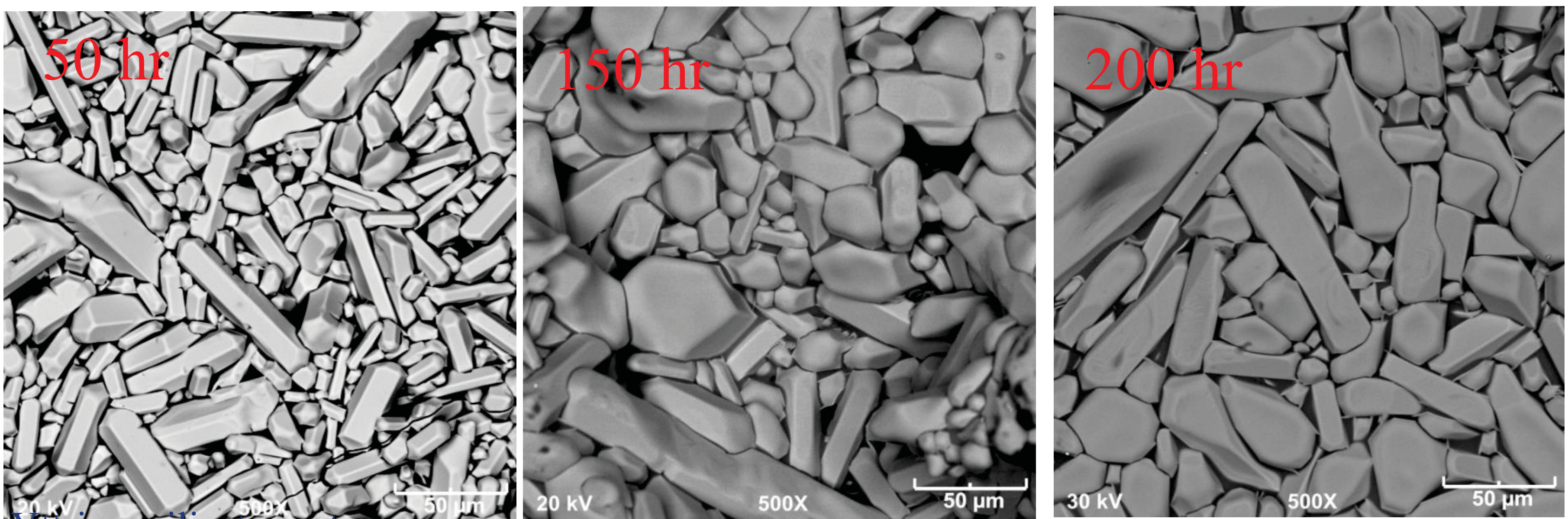


# Rare Earth Apatite Grain Growth

– Grain growth of apatite phase at 1500°C at various times



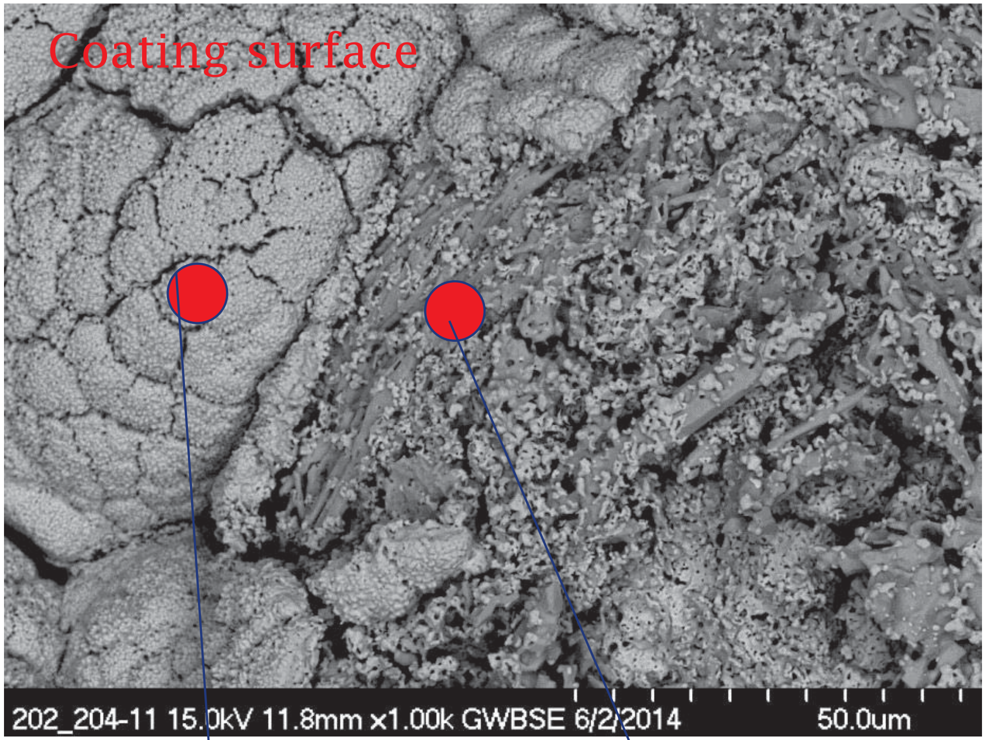

Ytterbium silicate system

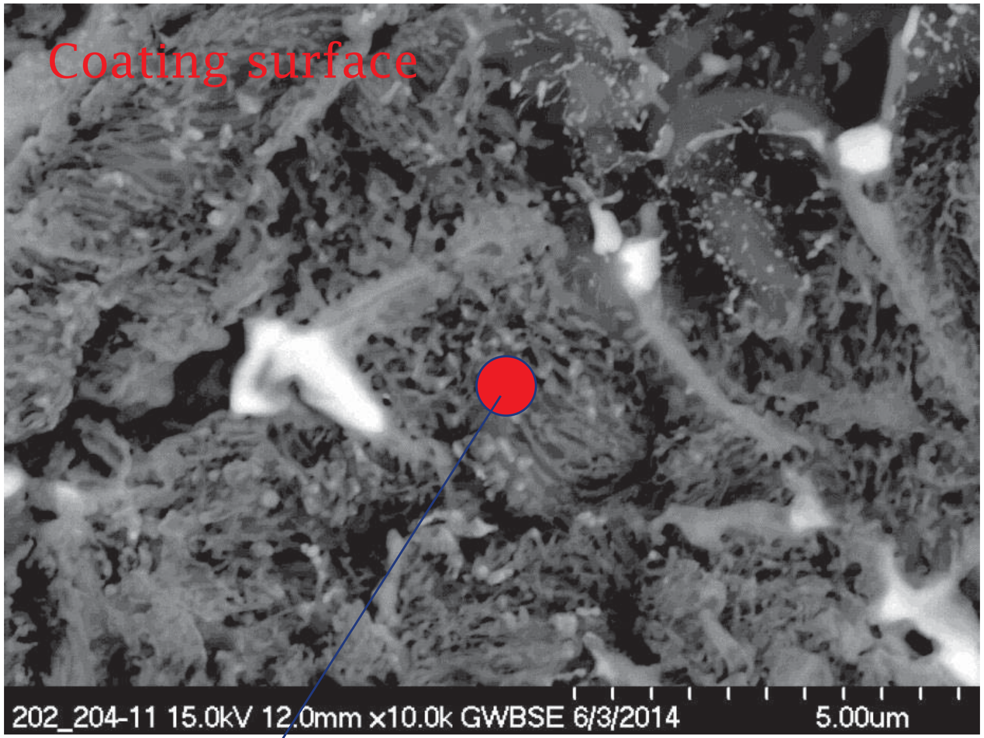



Yttrium silicate system

# $HfO_2$-Rare Earth Silicate Composite EBC Systems - Continued

– Silica loss observed in the concentrated CMAS reacted regions

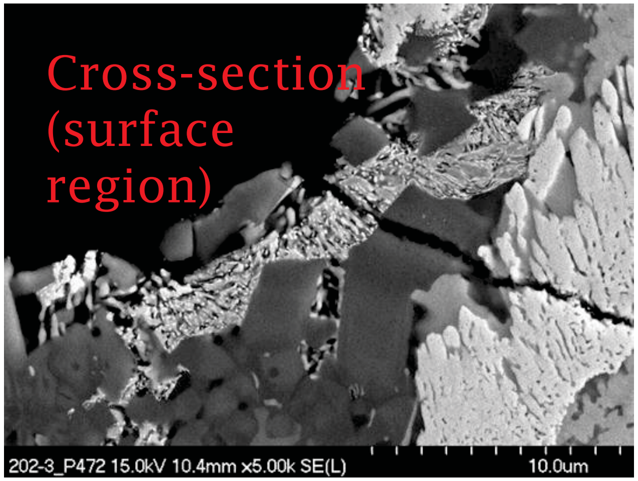



$HfO_2$ rich phase region

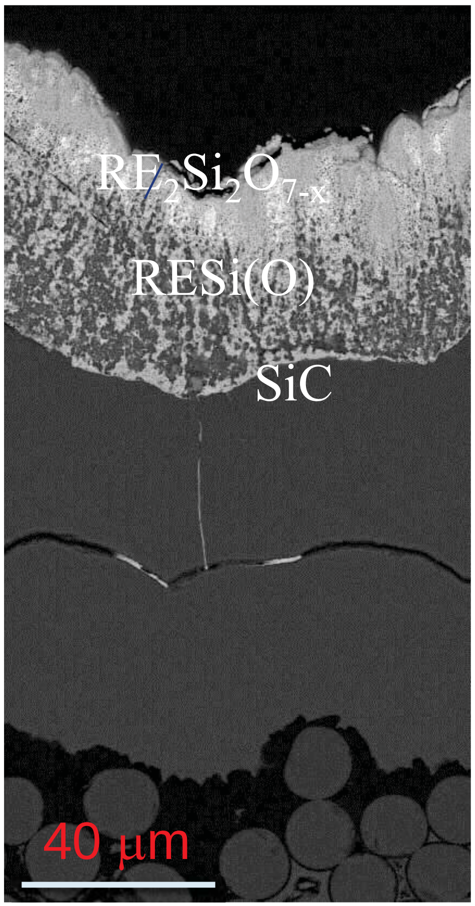
Rare earth silicate - apatite phase rich phase region

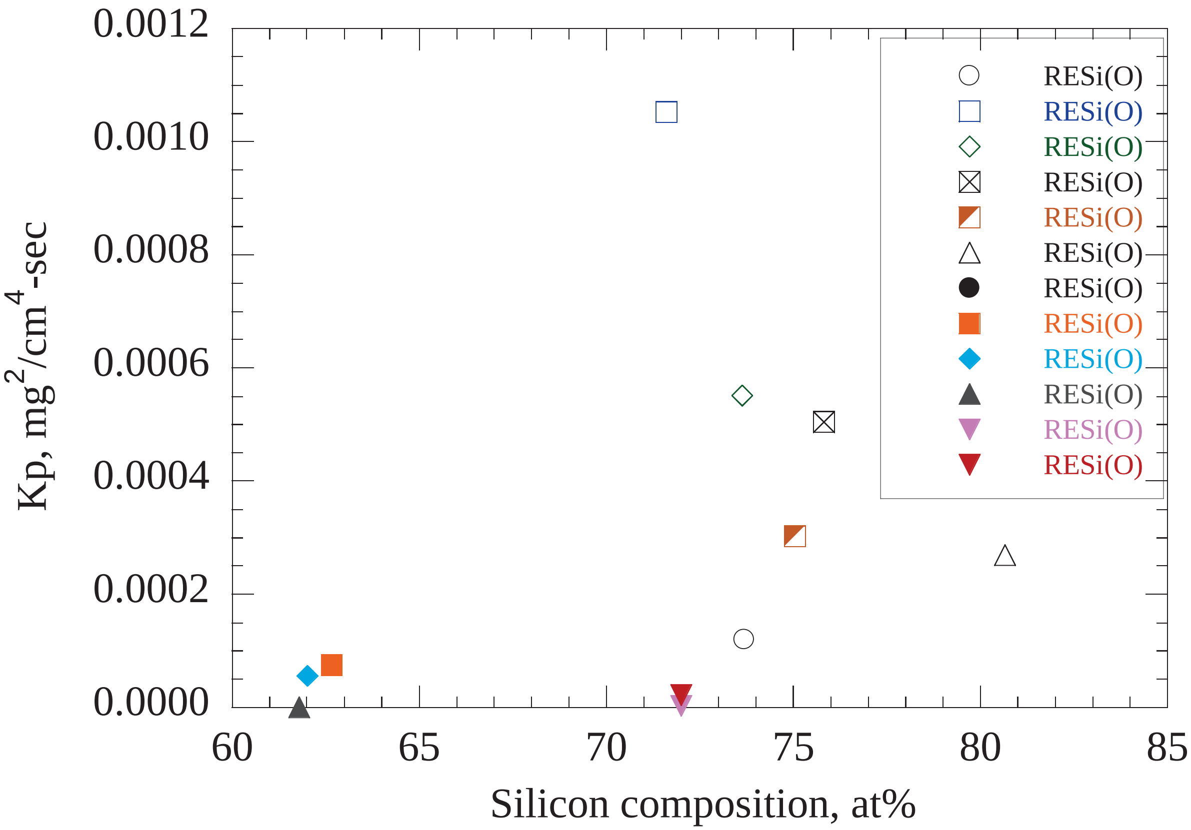
CMAS concentrated region, $SiO_2$ content 20-30 mol% ($SiO_2$ loss in the steam water vapor tests)



# High Stability Rare Earth Silicon Bond Coat with High Melting Point Coating Compositions: Designed with Improved Temperature capability and CMAS Resistance

- Thermogravimetric analysis (TGA) in dry $O_2$ at 1500°C, tested up to 500 hr
- “Protective” scale of rare earth di-silicate formed in oxidizing environments
- Furnace cyclic test life also evaluated at 1500°C

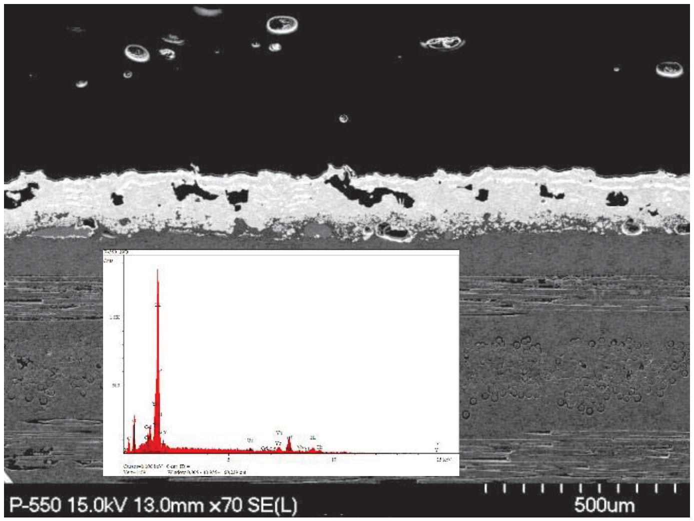


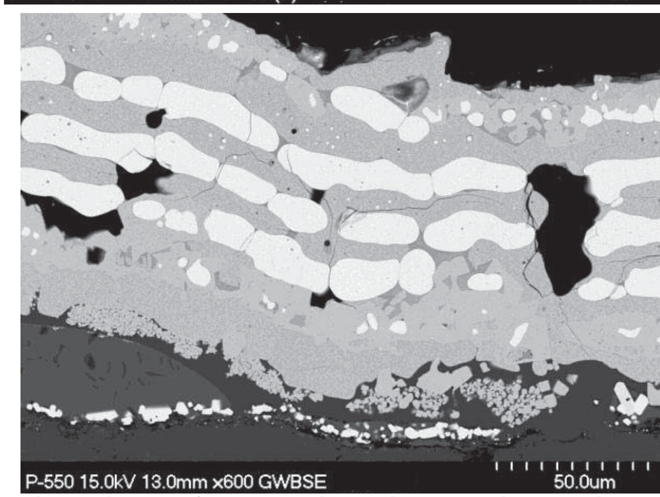




Oxidation kinetics vs Si content

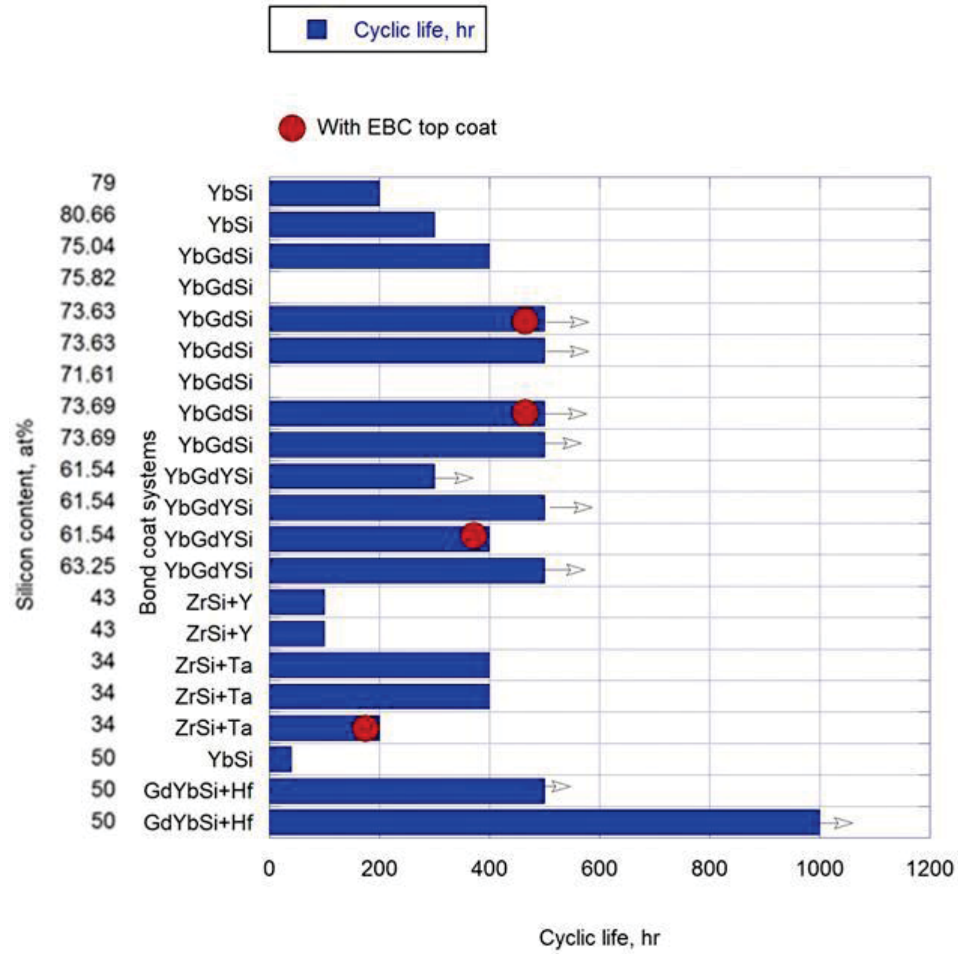
# High Stability Rare Earth Silicon Bond Coat with High Melting Point Coating Compositions: Designed with Improved Temperature capability and CMAS Resistance - Continued

- Thermogravimetric analysis (TGA) in dry $O_2$ at 1500°C, tested up to 500 hr
- “Protective” scale of rare earth di-silicate formed in oxidizing environments
- Furnace cyclic or high heat flux test life evaluated at 1500°C up to 1000 hours with or without CMAS



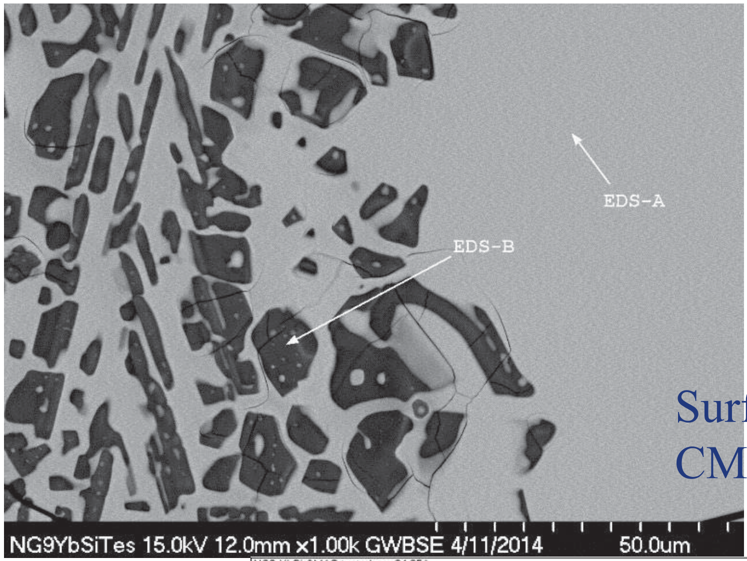

An Yb-Gd2700°F EBC bond coat showed 500hr cyclic durability



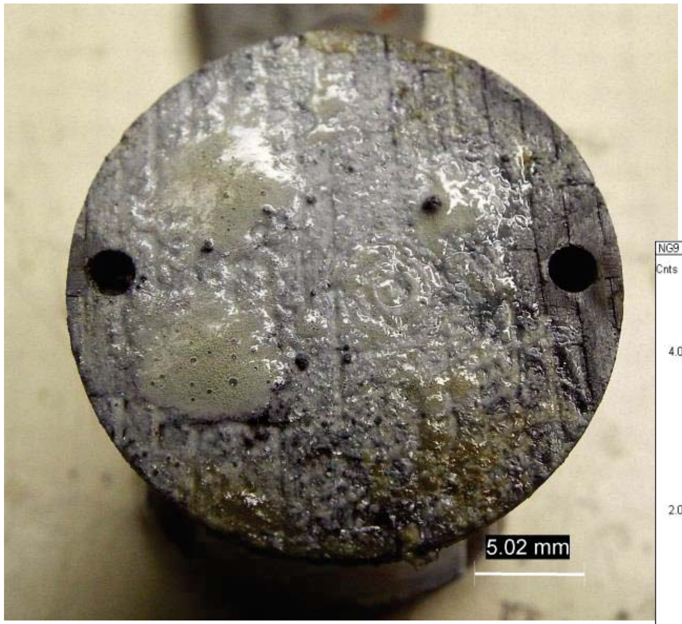

FCT life of RE-Si coatings

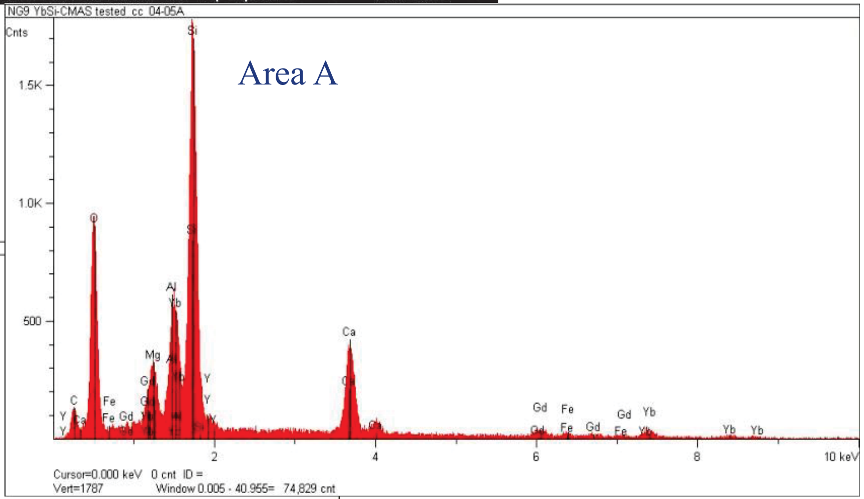
# High Stability and CMAS Resistance Observed from the Rare Earth Silicon High Melting Point Coating Compositions

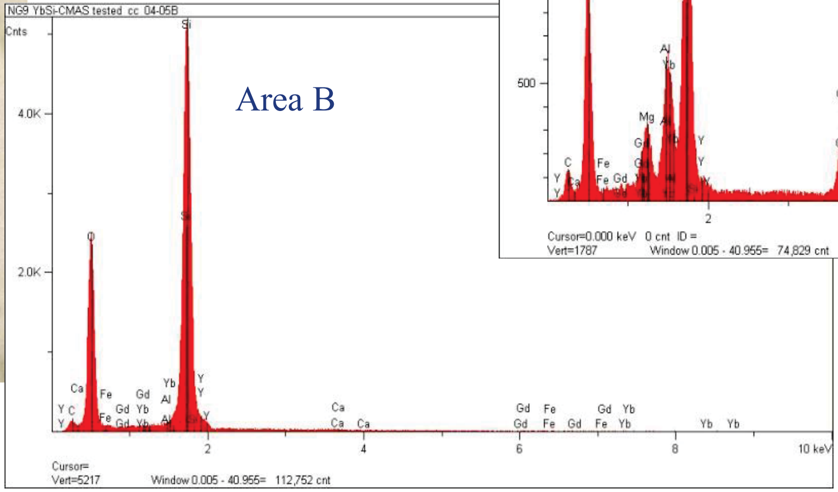
- Demonstrated CMAS resistance of NASA RE-Si System at 1500°C, 100 hr
- Silica-rich phase precipitation
- Rare earth element leaching into the melts (low concentration ~9 mol%)




Surface side of the CMAS melts



# CMAS Reaction Kinetics in Bond Coats

- $SiO_2$ rich phase partitioning in the CMAS melts
- Rare earth content leaching low even at 1500°C
- More advanced compositions are being implemented for improved thermomechanical – CMAS resistance

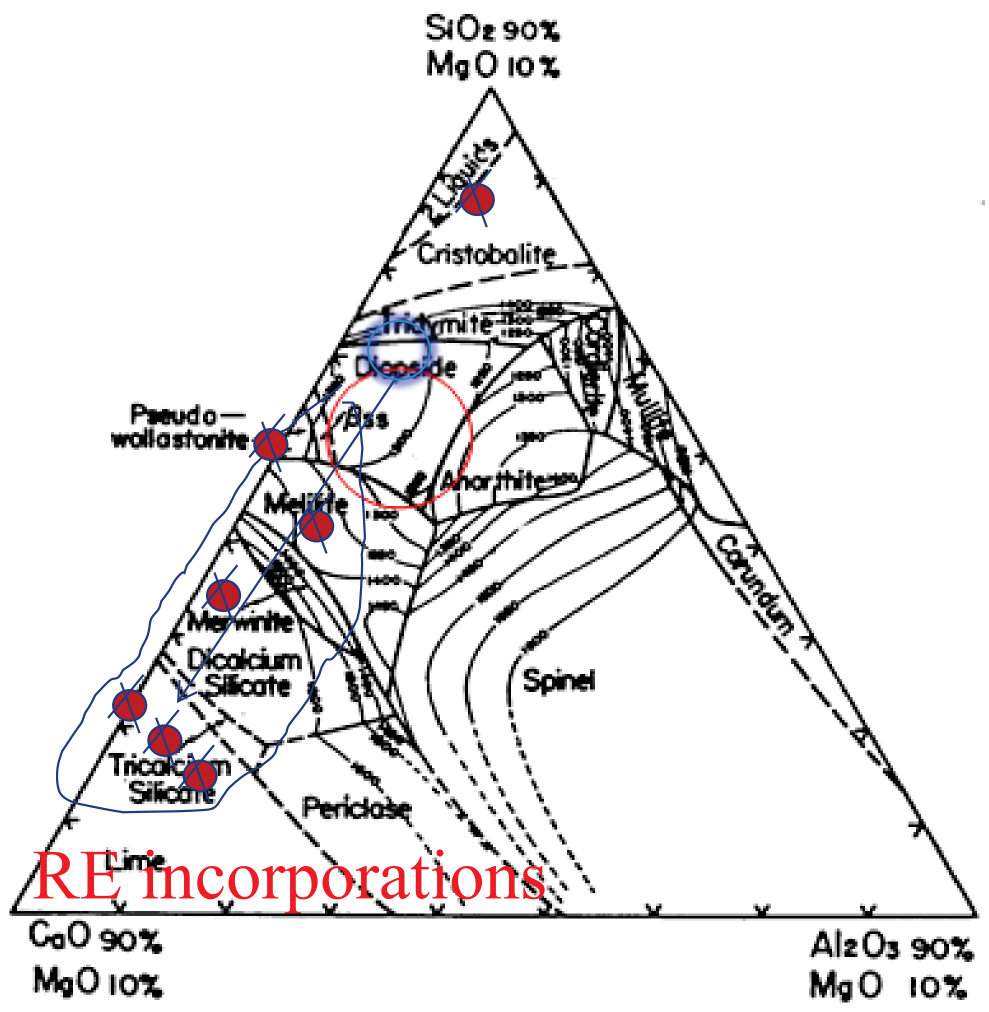
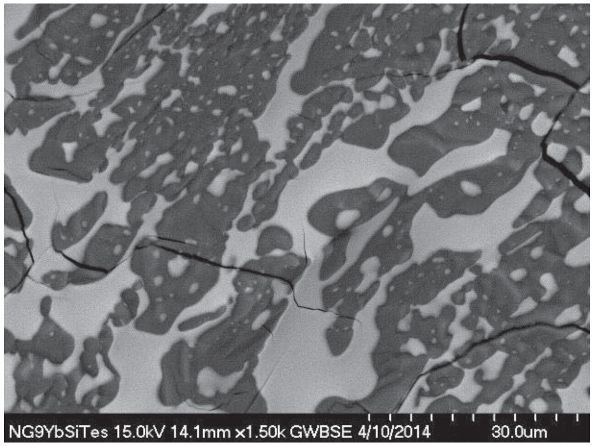



Fig. 4. The 10% MgO plane of the system CaO–MgO–$Al_2O_3$–$SiO_2$ showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

CMAS Partitioning on RE-Si bond coat, 1500°C, 100hr



# Advanced EBC Compositions Improve the Resistance to CMAS

– Controlling CMAS wetting, viscosity, stability and melting points
– Providing better EBC protections for CMCs in CMAS environments
– EBC durability being validated under CMAS-mechanical loading

400 hr, 69 Mpa creep rupture at EBC surface temperature 1400°C

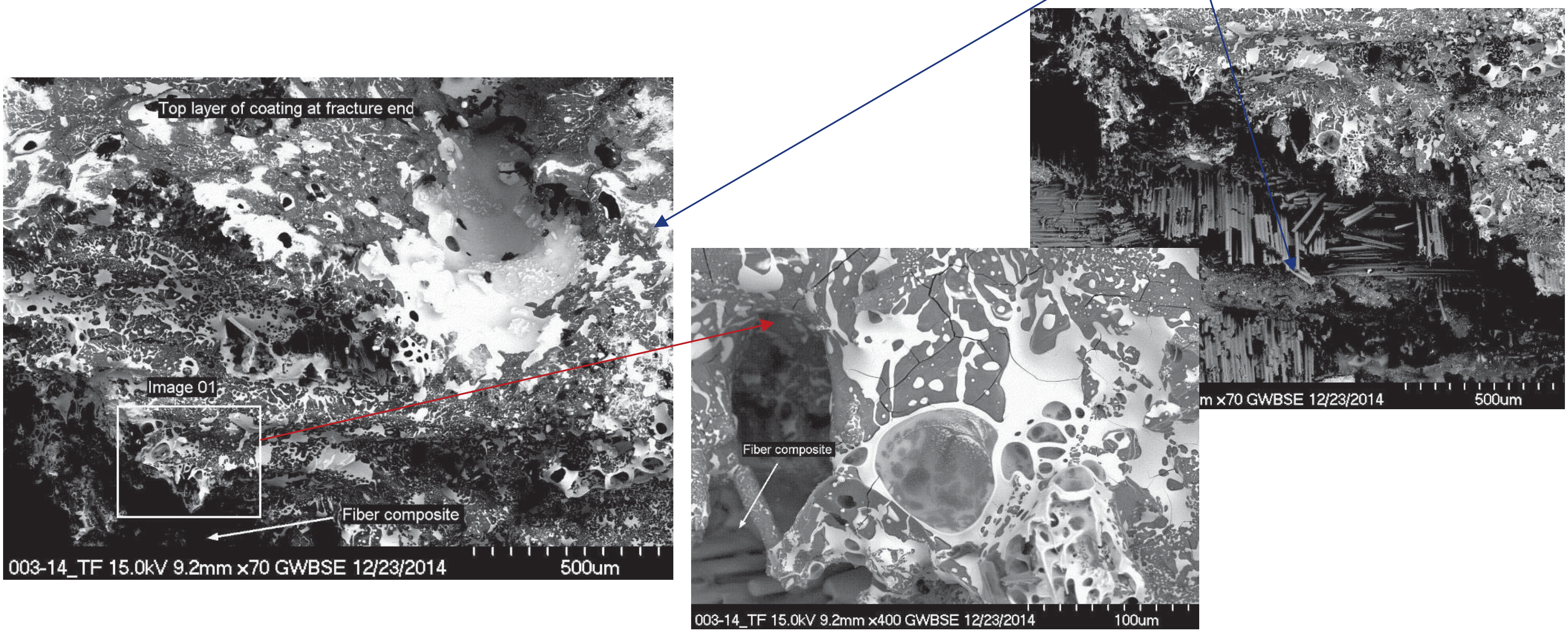
202 hr, 69 MPa creep rupture at EBC surface temperature 1540°C; CMC failure

# Advanced EBC Compositions Improve the Resistance to CMAS - Continued

- Controlling CMAS wetting, viscosity, stability and melting points
- Providing better EBC protections for CMCs in CMAS environments
- EBC durability initially validated under long-term CMAS-mechanical loading

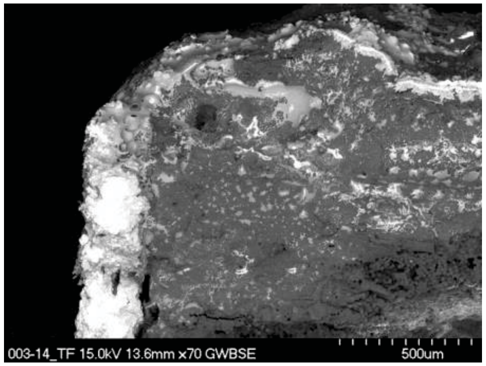
400 hr, 69 Mpa creep rupture at EBC surface temperature 1400°C

202 hr, 69 MPa creep rupture at EBC surface temperature 1540°C; CMC failure

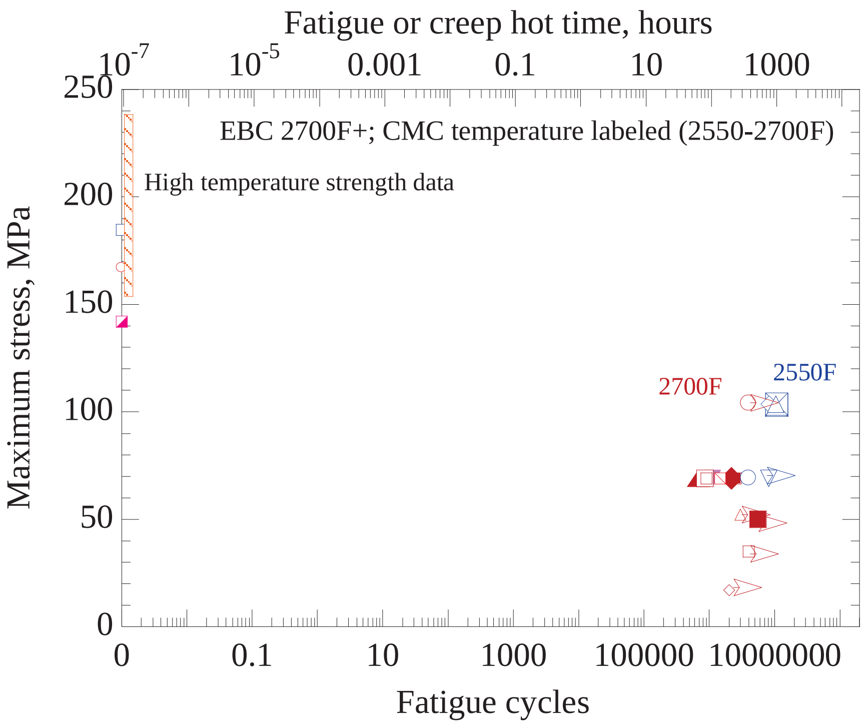


# Creep-Fatigue of EBCs-CMCs in Complex Heat Flux and Simulated Engine Environments

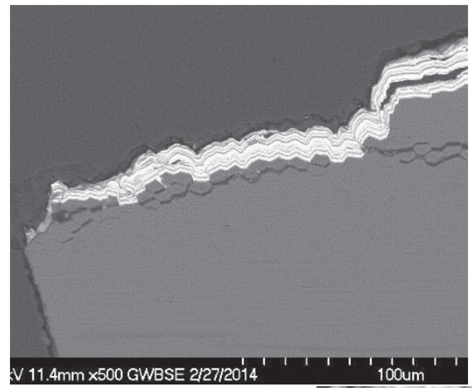
- Long-term creep and fatigue used to validate EBCs at various loading levels
- Demonstrated 2700°F EBC and bond coat capability in complex environments



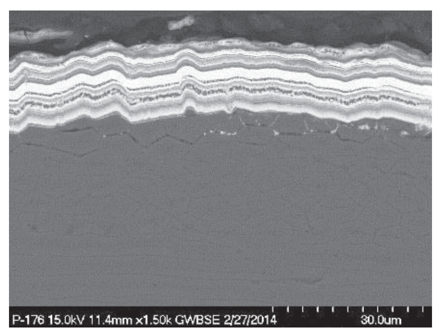

Fracture surface; 200+ hr at 2700°F+ creep rupture testing with CMAS; Advanced EBC protected CMCs

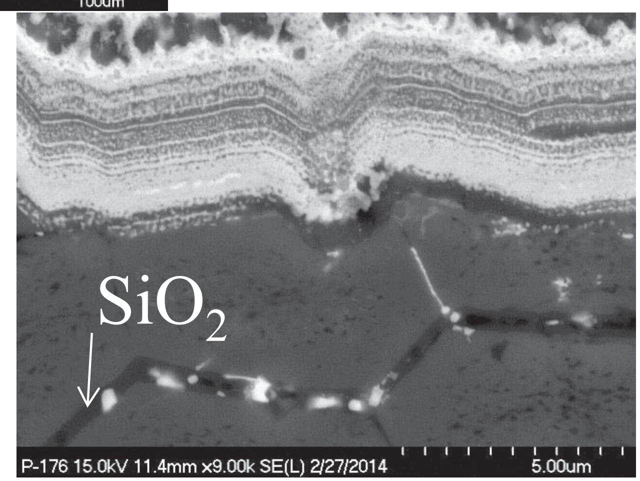



Stress-oxidation and stress-CMAS environmental testing




Advanced Bond Coat on CMC – intact after fatigue test with 15 ksi load and 2600-2700°F surface temperature for 460 hot hours




Advanced Bond Coat on CMC – intact after fatigue test with 15 ksi load and 2600-2700°F surface temp for 460 hot hours

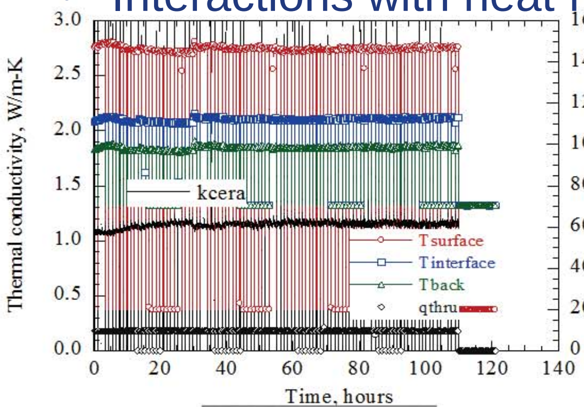
# Summary

- CMAS degradation remains a challenge for emerging turbine engine environmental barrier coating – SiC/SiC CMC component systems
- CMAS leads to lower melting point of EBC and EBC bond coat systems, and accelerated degradations
- NASA advanced EBC compositions showed promise for CMAS resistance at temperatures up to 1500°C+, and in combined with mechanical loading
- We have better understanding of CMAS interaction with rare earth silicates, and in controlling the compositions for CMAS resistance while maintaining high toughness
- We are developing better standardized CMAS testing, and working on CMAS induced life reductions, helping validate life modeling

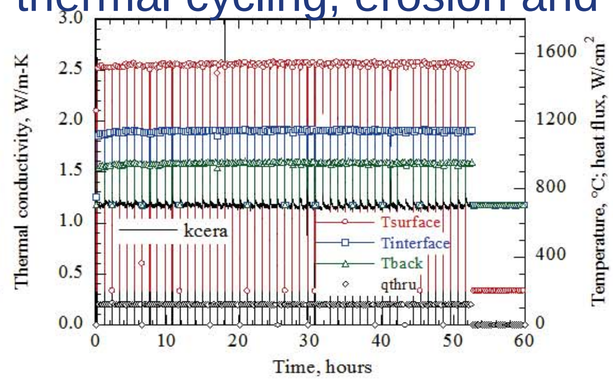
# EBC-CMAS Degradation under Thermal Gradients

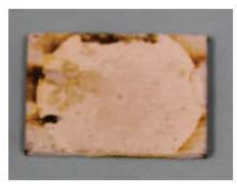
– **Effect of CMAS concentration on EBC-CMC system cyclic durability**

- CMAS reacts with high $SiO_2$ activity layer and reducing melting point
- Low tough reaction layers such as apatite phases
- Interactions with heat flux, thermal cycling, erosion and thermomechanical fatigue

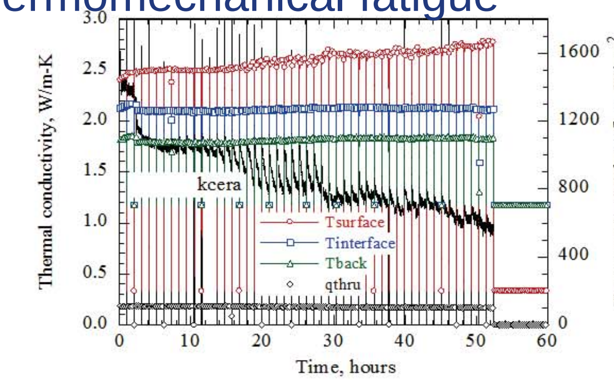



After 100 hr testing

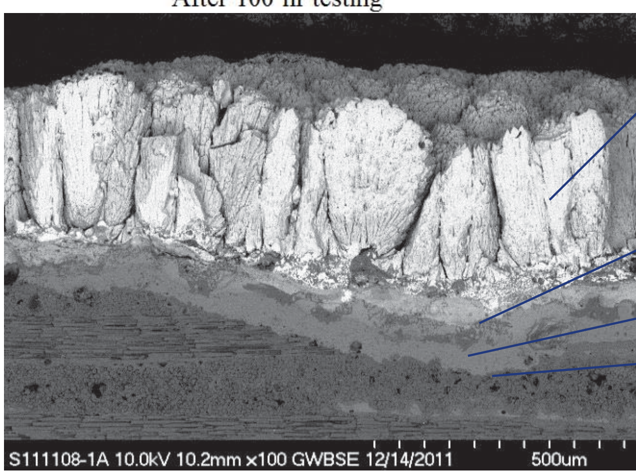


After 50 hr testing




After 50 hr testing

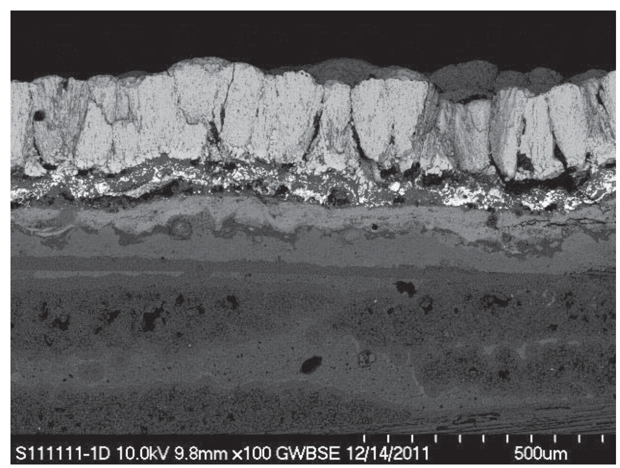



EB-PVD $ZrO_2$

$HfO_2$-$Yb_2O_3$-Aluminosilicate

$Yb_2Si_2O_7$

Si




More severe degradation and delamination: Tsurface 1500°C Tinterface 1316°C